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SOIL SCIENCE

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Contents

Fertility of a Soil as Related to the Forms of Its Iron and Manganese. P. H. BREWER AND R. H. CARR.....	165
Outgo of Calcium, Magnesium, Nitrates and Sulfates from High-Calcic and High-Magnesian Limes Incorporated in Two Soil Zones. W. H. MAC- INTIRE	175
Potassium Content of Plants as an Indicator of Available Supply in Soil. J. W. AMES AND R. W. GERDEL.....	199
Effects of Some Electrolytes on Kaolin and the Probable Relation to the Soil. JOHN R. SKEEN.....	225
Differences in the Heat of Reaction Between Artificial and Soil Gels of Silica, Alumina, and Iron, with Hydroxides. GEORGE JOHN BOUYOUCOS.....	243
Book Review.....	249
A Research Professorship in Forest Soils at Cornell University.....	251

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SOIL SCIENCE



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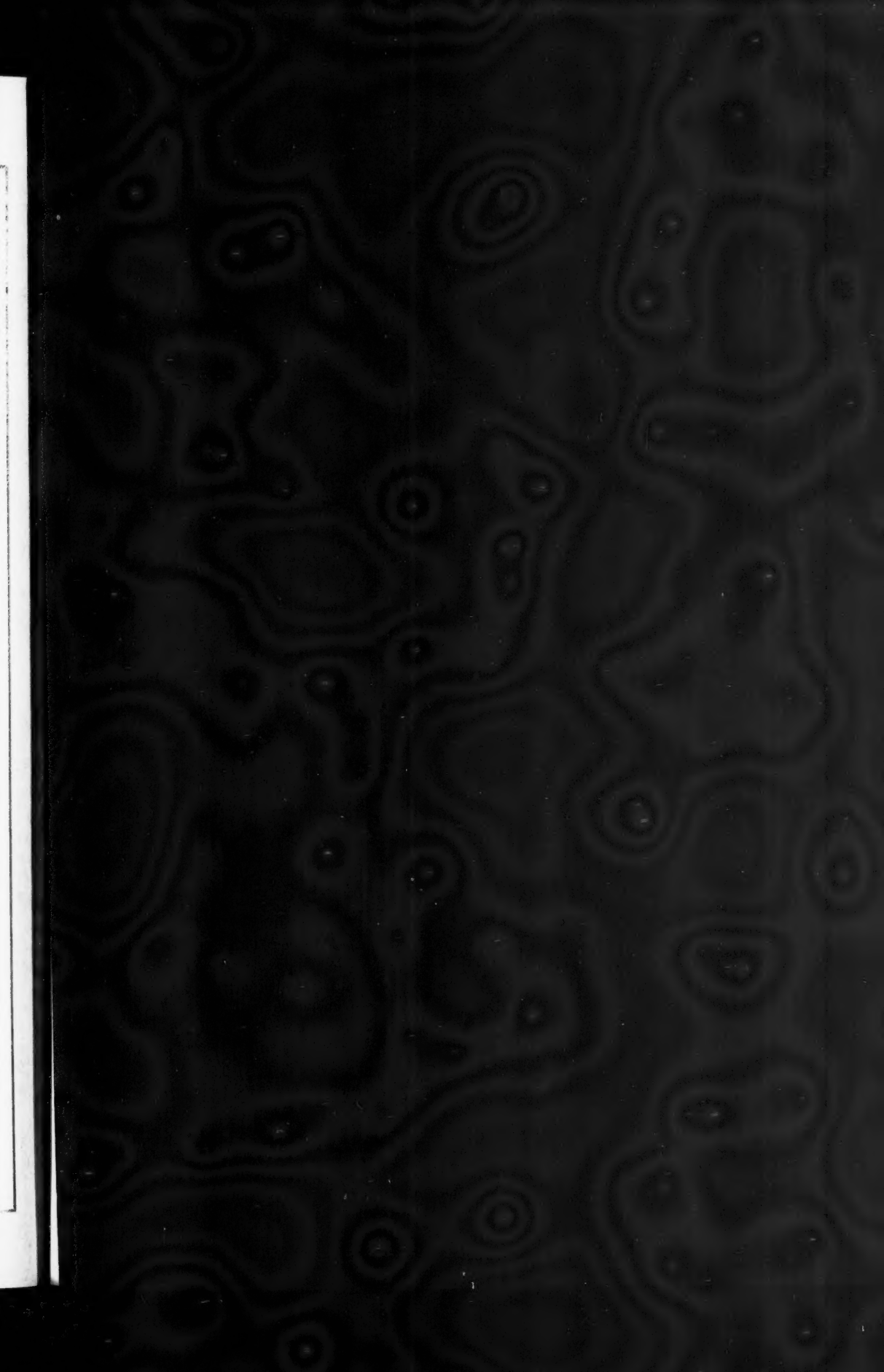
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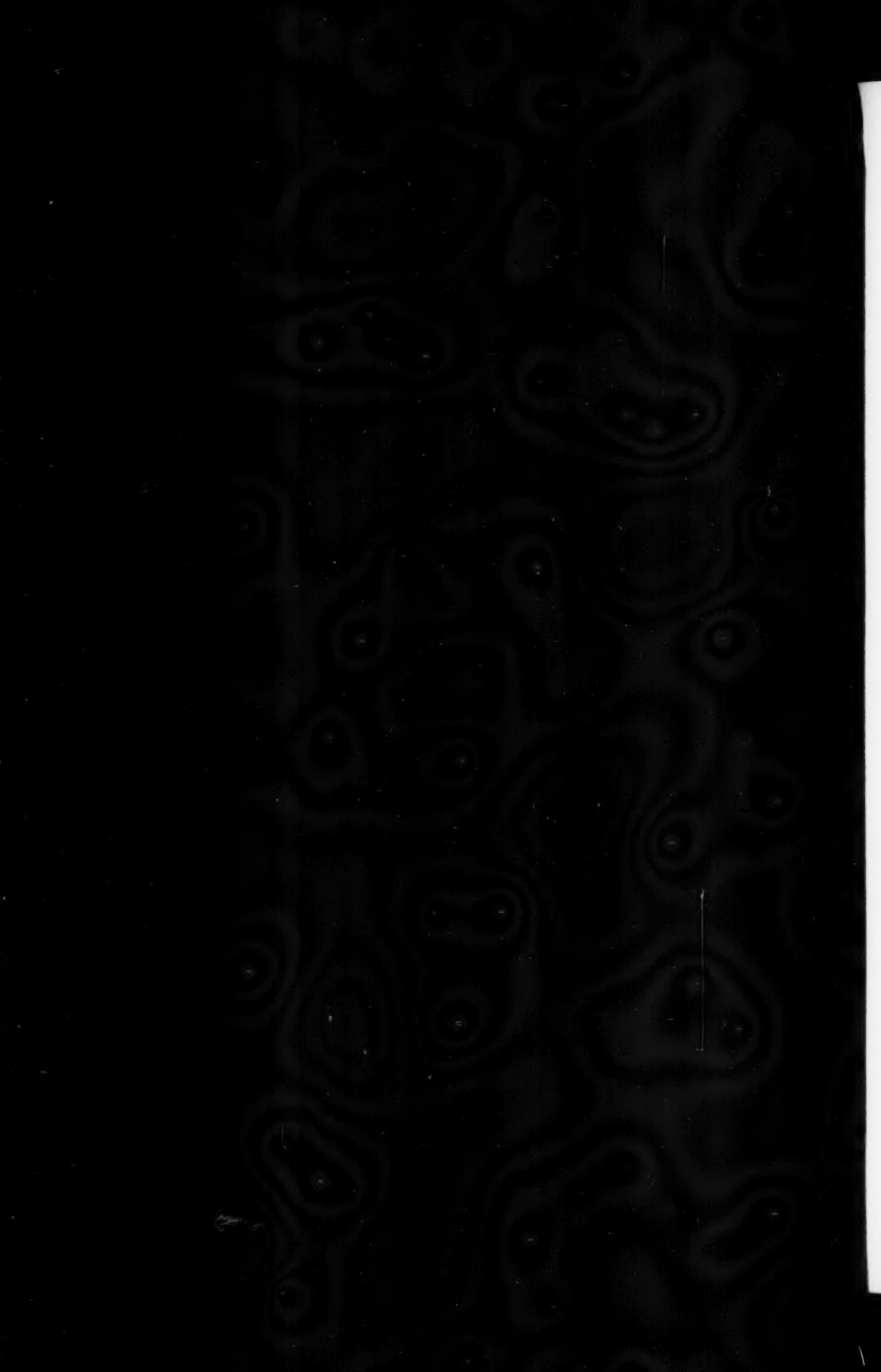
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FERTILITY OF A SOIL AS RELATED TO THE FORMS OF ITS IRON AND MANGANESE

P. H. BREWER AND R. H. CARR

Purdue University¹

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For a long time it has been known that many soils fail to give a good crop response, even after adequate applications of fertilizers containing nitrogen, phosphorus, and potassium, and after the correction of the acidity through the addition of limestone. The plants growing in these soils often give evidence of soil toxicity, such as by lack of suitable growth, yellowing of the leaves, and white stripes developing in the leaves. Evidence accumulating in recent years leads one to believe that the cause of the trouble is closely associated with the forms of the iron and manganese contained in the soil. It is well known that iron is essential to plant growth and it is believed that small amounts of manganese are also desirable and necessary (11) for good plant growth, but their relationship to soil toxicity and plant disease is a matter of more recent development.

EVIDENCE OF SIMILAR TOXICITY IN THE HAWAIIAN SOILS

The Hawaiian soils which are unusually high in iron and manganese have been investigated by Kelley (9), Johnson (8), McGeorge (10), and others, because of their toxicity to sugar cane and pineapple. A difference of opinion exists as to the real cause of pineapple chlorosis. McGeorge (11) believes the chlorosis found in the manganese soils "is due to a greater accumulation of lime indirectly caused by the presence of manganese in excessive amounts in the soil." Gile (7) found in Porto Rico that with heavy applications of stable manure to manganese soil containing about 30 per cent of lime it was possible to obtain a normal growth of pineapples, and Kelley in Hawaii found that this heavy manure treatment made it possible to obtain a good growth of pineapples on manganese soils.

FORMS OF IRON AND MANGANESE IN CERTAIN INDIANA SOILS

The presence of iron and manganese in forms which cause toxicity has been noted in many different soils in Indiana as well as in other states, but especially is this true of the experimental fields (11) near Bedford and Scottsburg, Indiana. It was thought worth while to study this latter area and to call atten-

¹Division of Agricultural Chemistry.

tion to the similarity of the treatments which have been helpful here and in the Hawaiian soils. The Scottsburg soil is what is known as "yellow clay" and responds well to manure treatment (as shown in plots 14 and 15, table 1),

TABLE 1
Limestone requirement, crop yields, and potassium thiocyanate color changes of the Scottsburg soils

PLOT NUMBER	LIME REQUIRED BY KCNS	COLOR* OF KCNS SOLUTION ON STANDING				TREATMENT	AVERAGE CROP YIELDS 1906-1922		
		1 hour	36 hours	60 hours	100 hours		Corn	Wheat	Clover
	<i>pounds</i>						<i>bushels</i>	<i>bushels</i>	<i>pounds</i>
1†	2,500	DR	DR	DR	DR	T	23.9	7.1	189
2†	2,300	DR	DR	DR	DR	T, NPK	32.2	12.7	364
3	1,300	R	R	R	R	L, NPK	36.2	13.6	468
4	1,400	R	R	R	R	L	22.9	6.9	288
5	900	R	LR	LR	LR	L, NPK‡	35.1	12.2	671
6	700	R	LR	LR	LR	L, NPK§	35.9	13.7	622
7	200	P	G	G	VG	Treatment changed 1920			
8	600	LR	P	VLG	VLG	L	27.0	8.4	457
9	100	P	C	G	VG	L, AP	35.0	12.4	655
10	2,000	DR	DR	DR	DR	O	20.6	6.9	274
11	1,800	DR	DR	DR	DR	AP	32.9	11.1	522
12	700	R	LP	C	G	L, RP	40.0	11.5	769
13	1,200	R	LR	P	VLR	L	28.7	8.0	509
14	1,200	R	P	G	VG	L, RP, M	53.5	17.5	1552
15	1,400	R	LP	LG	G	L, M	52.7	16.8	1344
16	900	LR	LG	G	VG	L	28.0	8.0	571
17	1,200	R	LR	G	VG	L, PK	38.0	14.0	854
18	1,100	R	LR	G	VG	L, NPK	39.4	16.9	713
19	1,100	R	LP	G	VG	L	27.6	8.0	475
20	900	R	LG	G	VG	L, NPK	40.3	16.1	815
21	1,000	R	LG	G	VG	L, NP	41.5	14.7	855
22	1,000	R	LP	G	VG	L	28.8	8.8	584

* P, pink; DR, dark red; LR, light red; C, colorless; G, green; VG, very green.

† Timothy instead of clover in rotation.

‡ Half of P from bone and half from acid phosphate.

§ P from steamed bone.

L—2 tons limestone per acre—1911.

M—10 tons manure on corn until 1919 lowered to 5 tons in 1920.

AP—150 pounds 16 per cent acid phosphate on wheat (began 1915); 150 pounds 16 per cent acid phosphate on corn.

RP—1 ton rock phosphate per acre 1905 also in 1911.

NPK—300 pounds 2-8-4 on wheat and additional; 300 pounds on corn beginning 1915.

but not well to complete fertilizer. As in the Hawaiian soils, the iron and manganese toxicity is not lessened much by liming, although the toxic aluminum has been largely overcome by this treatment as is shown by the lime

requirement. Other soils, such as that at North Vernon, with low organic content but with no appreciable amount of manganese in the dioxide form, usually respond well to treatment of commercial fertilizers, and good crop yields are obtained.

Table 1 shows the treatment and crop yield of the Scottsburg plots from 1906 to 1923. In addition, the limestone requirement by the quantitative potassium thiocyanate method (3) is given, as well as the effect of the presence of manganese dioxide upon the fading out of the red color of ferric thiocyanate.

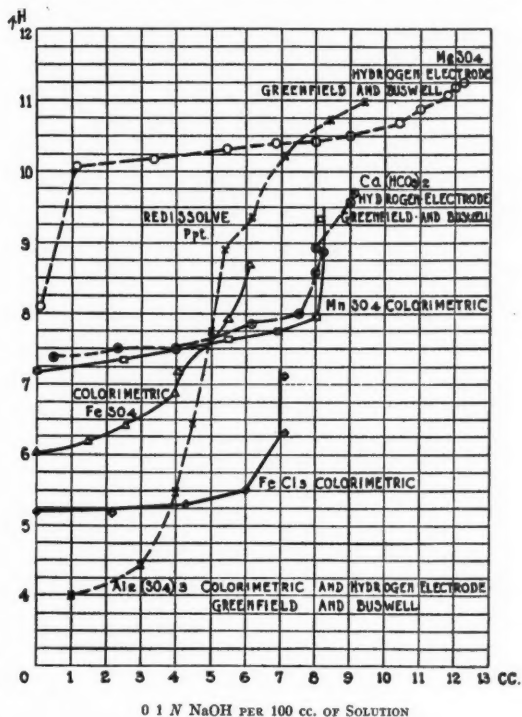


FIG. 1. PRECIPITATION OF ALUMINUM, FERRIC AND FERROUS IRON, MANGANESE AND MAGNESIUM AS HYDROXIDES AND CALCIUM BICARBONATE AS CALCIUM CARBONATE

(Indus. and Engin. Chem. 15: 634)

It will be noted from table 1 that the crop increase due to the use of manure in plots 14 and 15 was considerable, and that no combination of commercial fertilizers produced similar yields. The addition of rock phosphate made little improvement over manure in the crop yield in plot 14. Hence it is evident that the organic matter was able to correct, to a considerable extent,

the toxicity which the application of complete commercial fertilizers did not greatly alter. One important reason for the great crop increases in plots 14 and 15 is believed to be the reduction, by the rotting manure, of some of the manganese dioxide and some of the ferric iron to the ferrous form, in which condition iron remains in solution and available to the plant when the reaction of the soil is less acid than pH 5.5 as previously shown by the writers (fig. 1). It is believed by Johnson (6) that the improved pineapple growth reported in the Hawaiian soils from the addition of manure was due to the availability of the iron reduced from the ferric to the ferrous condition by the manure. It will be noted from figure 1 that ferrous iron is not easily precipitated as a hydroxide and seems to be available to plants even when the soil is about pH 8.

METHODS OF DETERMINING MANGANESE DIOXIDE AND FERROUS IRON IN SOIL

In this investigation one of the methods used to determine manganese dioxide quantitatively in the soil was a modified Bunsen method in which hydrochloric acid is added to the soil, the liberated chlorine is distilled into a

TABLE 2
Showing the weight of manganese dioxide added to five-gram samples of soil, and the amounts recovered

SOIL NUMBER	MnO ₂ ADDED	MnO ₂ RECOVERED	DIFFERENCE
	gm.	gm.	
1	0.1531	0.1521	0.0010
2	0.1392	0.1347	0.0045
3	0.1516	0.1436	0.0080
4	0.1392	0.1384	0.0008
5	0.1531	0.1476	0.0055
6	0.1516	0.1436	0.0080

potassium iodide solution, and the free iodine thus formed is treated with standard sodium thiosulfate. Since organic matter in the soil seriously interferes with chlorine liberation, different compounds were tried to get rid of this interference as much as possible. The addition of 0.2 gm. of mercuric oxide to 5 gm. of soil was found to be fairly successful. This causes some kind of a combination between the mercury and organic material when boiling with the hydrochloric acid. The mercury-organic compound could be seen moving about in the form of "balls" in the boiling mass. In order to test the accuracy of this method, a known amount of manganese dioxide was added to each of a series of different soil types having an organic content from three to seven per cent (manganese dioxide was not found in soils high in organic matter) and then an attempt was made to recover it. The data thus obtained are given in table 2.

FERROUS AMMONIUM SULFATE METHOD OF DETERMINING MANGANESE DIOXIDE
IN SOIL

Manganese dioxide in soil was determined more satisfactorily by use of a ferrous ammonium sulfate method as follows:

Five grams of soil and 100 ml. of a 5 per cent solution of ferrous ammonium sulfate to which had been added concentrated sulfuric acid at the rate of 6 ml. to the liter were placed in a tall shaker bottle of about 200 ml. capacity. The soil and solution were thoroughly mixed and the bottle was then placed in boiling water for 30 minutes. The soil and solution were mixed by shaking several times during the digesting period. After the digestion had been completed the bottle was placed in an upright position and allowed to remain until the soil had settled. Twenty-five-milliliter samples were pipetted off into 250-ml. Erlenmeyer flasks, and 50 ml. of water, 25 ml. of concentrated nitric acid, and about $\frac{1}{2}$ gm. of sodium bismuthate were added and the contents boiled slowly for about ten minutes. If the red color of the sodium permanganate disappeared, more sodium bismuthate was added and the contents were boiled again. This process was repeated until the red color remained after 5 minutes of gentle boiling. A few milliliters of 5 per cent sodium nitrate solution was added to reduce any manganese dioxide that may have formed during the boiling. The flask was next cooled to room temperature and about 0.4 gm. of sodium bismuthate was again added. The flask and contents were allowed to stand for 15 to 20 minutes so that all the manganese would be oxidized to permanganate. The contents of the flask were filtered through an asbestos filter, washed, and the filtrate was titrated at once with standard sodium arsenite.

DETERMINATION OF SOLUBLE MANGANESE (OTHER THAN MANGANESE DIOXIDE)
AND THE FERROUS IRON IN A SOIL

It has been shown by Mitschek (13) that 0.27 *N*, H_2SO_4 does not dissolve manganese dioxide. This has been verified by the writers as shown by data in figure 2. The easily soluble manganese in the soil (other than manganese dioxide) and the ferrous iron were dissolved by heating 10 gm. of 100-mesh soil with 200 ml. of 0.2 *N* H_2SO_4 in boiling water for 30 minutes. When cool, aliquots were taken for the determination of manganese as given above (leaving out the ferrous ammonium sulfate). The ferrous iron was determined by titrating an aliquot with 0.1 *N* potassium dichromate using diphenolamine as the indicator. Data obtained by this method checked fairly well with the Bergeim (2) method of obtaining ferrous iron in feces. The results obtained by the various methods just described are given in table 2.

GREEN COLOR OF POTASSIUM THIOCYANATE SOIL SOLUTION AS AN INDICATOR OF
MANGANESE DIOXIDE

In a previous article (4) the writers called attention to the green color when determining the limestone requirement by the quantitative potassium thiocyanate method (3) and attempted an explanation of the cause of the red color fading out when the Comber (5) qualitative method for soil acidity was used on soils. A method to obviate the fading out of the red color in this process has been suggested by Emerson (6). He concludes that the fading out is due to the presence of soluble phosphates and has developed a solution for testing

soils in which the interfering phosphate is first precipitated. This method, however, was used on the soils noted in table 1, as well as on many other soils containing manganese dioxide, and, as when the Comber solution was used, the red was found to fade out or become less red depending on the amount of manganese dioxide. This would indicate some other cause for this fading out.

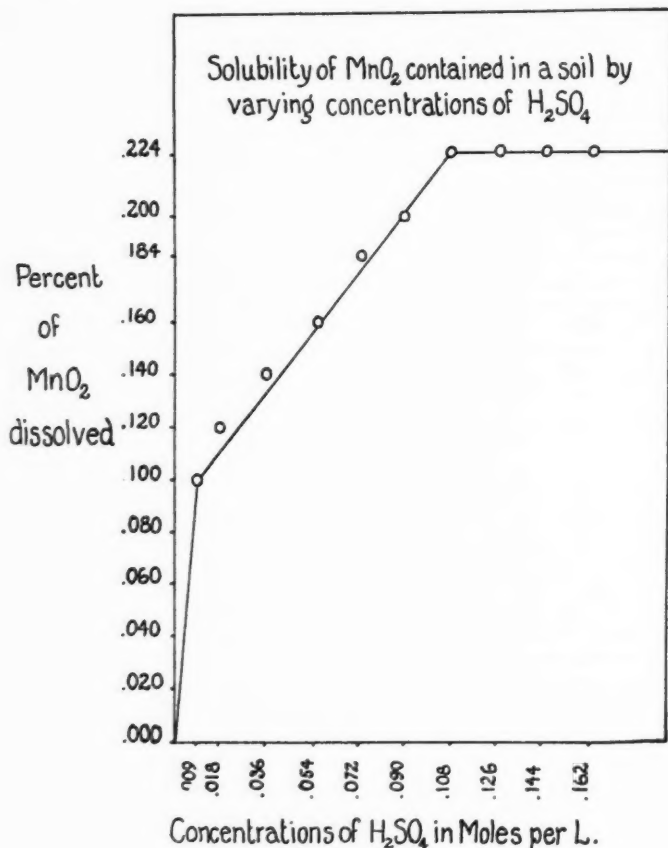


FIG. 2

NATURE OF THE GREEN MANGANESE SOLUTION

McGeorge (11) has taken exception to a statement of the writers relative to the pH at which manganese is precipitated as a hydroxide from salts of manganese and from the potassium thiocyanate compound in alcohol. The difference of opinion seems to be a question of solution vs. colloidal suspension

of the manganese compound. The writers believe, in contradistinction to McGeorge, that the green color of the KCNS solution is not due to a definite chemical compound, but largely to a colloidal suspension containing manganese which causes a scattering of light, as shown by the strong Tyndal cone effect observed in the green liquid. Anderegg and Lutz (1) believe that this colloidal suspension is produced by the mutual effect of oppositely charged colloids, such as the absorption of the positive ferric iron by the negative manganese

TABLE 3
Amounts of ferrous iron and manganese dioxide obtained by the various methods

PLOT NUMBER	MnO ₂ BY BUNSEN'S METHOD	MnO ₂ † BY Fe(NH ₄) ₂ (SO ₄) ₂ PLUS H ₂ SO ₄ (A)	MnO ₂ * BY H ₂ SO ₄ (B)	DIFFERENCE IN MnO ₂ (A - B)	Fe IN H ₂ SO ₄ ‡
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
1	0.065	0.200	0.116	0.084	0.106
2	0.068	0.180	0.120	0.060	0.106
3	0.055	0.174	0.084	0.090	
4	0.055	0.160	0.084	0.076	
5	0.054	0.188	0.140	0.048	0.112
6	0.053	0.200	0.136	0.064	0.112
7	0.087	0.208	0.142	0.062	0.106
8	0.060	0.204	0.128	0.076	0.106
9	0.065	0.244	0.180	0.064	0.095
10	0.060	0.232	0.180	0.052	0.106
11	0.075	0.224	0.136	0.086	0.106
12	0.073	0.240	0.194	0.056	0.127
13	0.056	0.244	0.184	0.060	0.127
14	0.026	0.236	0.200	0.036	0.191
15	0.030	0.268	0.244	0.044	0.191
16	0.066	0.284	0.152	0.132	0.095
17	0.076	0.296	0.188	0.108	0.106
18	0.064	0.326	0.184	0.136	0.106
19	0.065	0.320	0.176	0.144	0.085
20	0.074	0.328	0.184	0.144	0.095
21	0.068	0.356	0.232	0.124	0.106
22	0.077	0.324	0.204	0.120	0.085

* Manganese other than manganese dioxide.

† Total manganese.

‡ Data obtained by C. H. Keipper, unpublished.

dioxide or by such other negative colloids as Fuller's earth or Putman's clay. Analyses of the green KCNS compound in alcohol show the presence of large amounts of manganese. The pH had been previously determined by the colorimetric method, but has been repeated electrometrically recently with other soil types, by the use of the quinhydrone electrode. The results show that the liquids with the green suspension have a pH of about 6, and that all were still somewhat green at pH 8.5, after the additions of successive increments of 0.1 *N* alcoholic potassium hydroxide.

CAUSES OF THE FADING OUT OF THE RED COLOR OF FERRIC THIOCYANATE

It is well known that a basic solution of soluble phosphate will combine with and displace the iron of the ferric thiocyanate ($\text{Fe}(\text{CNS})_3$) compound, but it is believed by the writers that there is usually no appreciable amount of soluble phosphate present in a wet or moist soil at the same time with easily soluble ferric iron available to form ferric thiocyanate. If such were the case they would soon combine in the soil to form iron phosphate.

It is possible to take out the red color of $\text{Fe}(\text{CNS})_3$ from a soil solution in various ways, as, in some cases, by adding water; soil containing MnO_2 ; MnO_2 in pure form; soluble bases or phosphates, borates, or arsenates; or many organic acids such as oxalic, tartaric, citric, and malic. On the other hand, the red color may be restored by adding a ferric salt in excess of the MnO_2 , or by lowering the pH to dissolve more iron.

DISCUSSION

It will be noted from table 1 that in plots 14 and 15 there is less MnO_2 in the soil, and that more of the iron is in the ferrous form, than in any of the other plots. It will be noted also in table 1 that in plots 1 to 4, and 10 to 11, to which there had not been enough lime or phosphate added to precipitate the iron as a hydroxide or phosphate, the red did not fade out, but in all the others the red color disappeared in about 36 hours, the solution became colorless, and a very green color developed in about 100 hours. It is thus evident that the shade of red (or green) obtained by the Comber method in testing manganese soils is determined not only by the amount of base or phosphate compound present but also by the extent to which the ferric iron is in excess of the manganese dioxide in the soil sample. As one of the writers (3) has previously pointed out, the use of the KCNS color standard alone as a guide to the lime requirement of a soil, is, therefore, not reliable.

SUMMARY

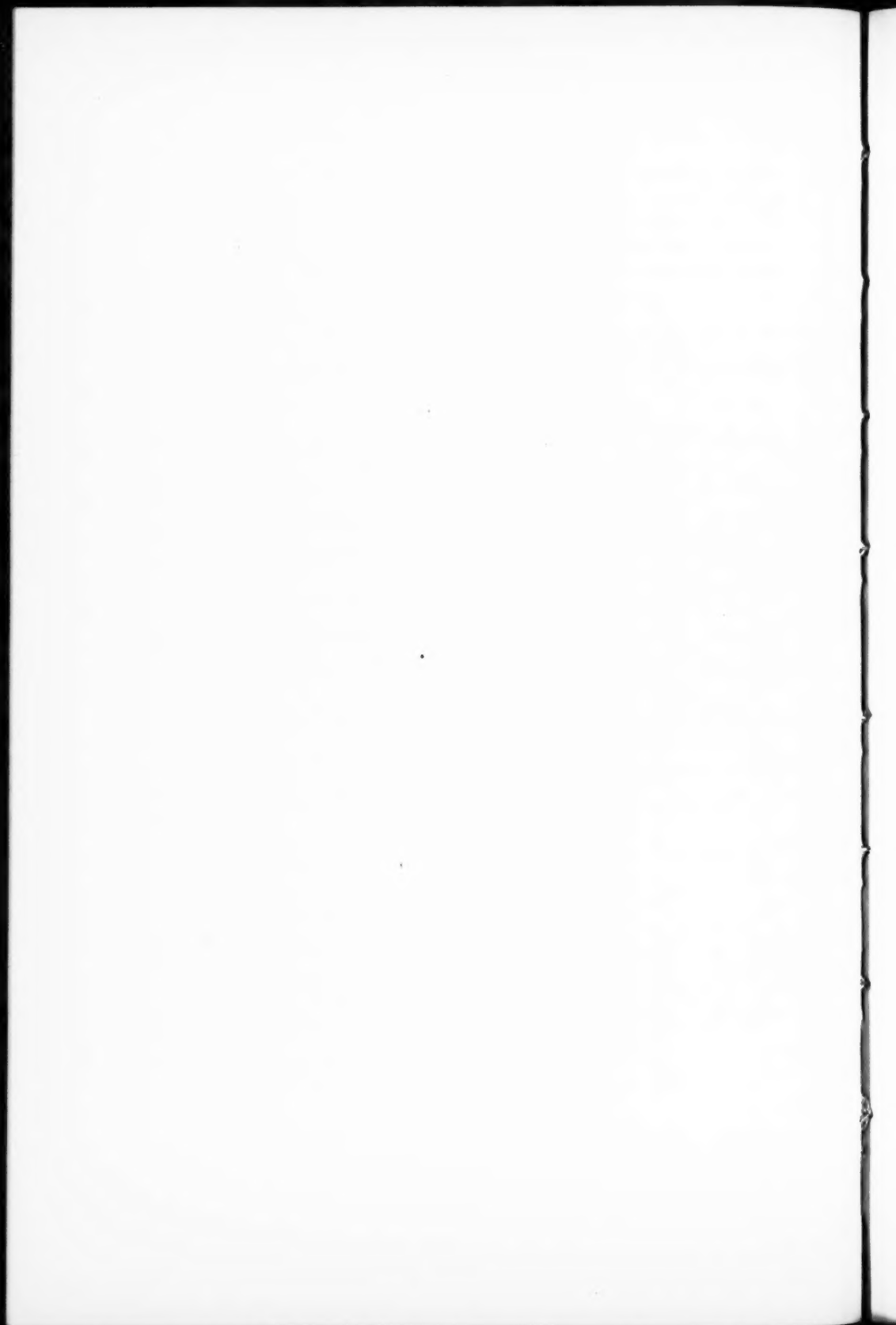
A study of the different plots of the Scottsburg experiment field indicates that a toxic substance is present in the soil and that the iron present is mostly in the ferric condition. The conditions in the soil which cause the oxidation of the manganese to the dioxide form also change most of the ferrous iron to ferric, in which form it is not available to plants when the acidity is about pH 6.0. This condition is counteracted to a considerable extent by the reducing action of manure but not by commercial fertilizers. The manure added to the soils studied did not greatly change the percentages of iron and manganese present in the soil, but their less oxidized forms seem to be more favorable to plant growth. This change is believed to have been the main cause for an annual increase of about one-third in the corn and wheat yields and an approximate doubling of the clover yield.

The presence of manganese dioxide can usually be recognized by the forma-

tion of a green color when the soil is tested by the quantitative potassium thiocyanate method for acidity. The manganese dioxide often present in soil will cause a fading out of the red color of $\text{Fe}(\text{CNS})_3$, if there is less available iron than manganese (MnO_2) present. The KCNS color standard method thus may indicate a basic soil, whereas in reality the soil is acid.

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OUTGO OF CALCIUM, MAGNESIUM, NITRATES AND SULFATES FROM HIGH-CALCIC AND HIGH-MAGNESIC LIMES INCOR- PORATED IN TWO SOIL ZONES

W. H. MacINTIRE¹

University of Tennessee Agricultural Experiment Station

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Although soil literature is replete with comparisons between calcium and magnesium in their more active forms, very little attention has been paid to the effects produced by joint additions of these two elements in the proportions approximating those found in magnesian limes. Insufficient consideration has been accorded the possible antagonistic effects between calcium and magnesium *after* their joint absorption from near-equal additions. It has been generally assumed that preponderant additions of either calcium or magnesium result in reciprocal liberations in the soil; but it has been demonstrated that such an interchange may not follow when either caustic or carbonate forms are incorporated throughout the surface soil. When measured by the rainfall leachings *under humid conditions* (6, 7), liberation not only failed to occur in certain surface soils, but calcium and magnesium incorporations were reciprocally repressive upon native soil complexes of magnesium and calcium. The reverse was found in the case of subsoil (6). There the slowly moving nitrate- and sulfate-impregnated solutions did effect an interchange, which was influenced by concentration of the neutral salts of one element, irrespective of an accumulation of the carbonate of the same element in the subsoil through deposition from its bicarbonate carried by soil leachings (6). Hence, not only may the soil solution be altered in its proportion of dissolved Calcium and Magnesium as a result of increase of the element added in excess, but the change in proportion may be further accentuated through repressed solubility of the soil's content of the other element.

Although high-calcic lime, precipitated CaCO_3 , and limestone may decrease the outgo of magnesium from the surface soil when the additions are mixed throughout the full depth of soil, and although MgO , precipitated MgCO_3 , and magnesite may effect a similar decrease in calcium outgo, an increase in the outgo of both calcium and magnesium may or may not, come from full-depth incorporations of dolomite (6, 7) at different rates. One Ca:Mg proportion obtained in the leachings when the dolomite underwent complete

¹ The results were obtained by Mr. H. Stanford, Mr. T. D. Harden, and Dr. R. M. Barnette all of whom were formerly employed as assistants through an endowment from the National Lime Association, with equipment donated by the American Limestone Company.

TABLE 1
Total calcium, magnesium, and calcium-magnesium leached during 4 years from 2,000-pounds CaO equivalents (3,570 pounds CaCO_3) of hydrated lime, burnt dolomite, and mixture of separately calcined CaO and MgO incorporated in the surface zone of a loam soil—terms of CaCO_3 -equivalence per 2,000,000 pounds of moisture-free soil

TREATMENT	FIRST YEAR					SECOND YEAR					THIRD YEAR					FOURTH YEAR					TOTAL FOR 4 YEAR PERIOD		4-YEAR INCREASE IN OUTGO OVER CONTROLS	
	May to September	September to January	January to March	March to May	Total	May to December	December to February	February to May	Total	May to September	September to February	February to May	Total	May to December	December to May	Total	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	Actual	On basis of addition
Calcium as CaCO ₃ ⇌																								
Controls.....	128	136	53	40	357	108	43	37	188	69	81	27	177	126	50	176	898
Ca(OH) ₂	240	201	55	47	543	138	43	39	220	79	82	27	188	149	41	190	1,141	243	6.8
CaO-MgO*.....	214	204	52	36	506	113	41	34	188	88	83	24	195	136	41	177	1,066	168	7.9†
CaO-MgOH*.....	150	223	53	46	472	122	43	36	201	75	73	27	175	128	36	164	1,012	114	5.4‡
Magnesium as CaCO ₃ ⇌																								
Controls.....	34	39	18	20	111	34	20	20	74	31	32	14	77	43	31	74	336
Ca(OH) ₂	59	52	16	17	152	38	21	21	80	24	26	15	65	43	24	67	364	28
CaO-MgO*.....	53	56	16	17	138	37	20	21	78	32	39	18	89	59	35	94	399	63	4.3†
CaO-MgOH*.....	37	56	17	20	130	41	21	21	83	24	32	18	74	60	31	91	378	42	2.9‡

Calcium-magnesium as $\text{CaCO}_3 \rightleftharpoons$

Controls.....	162	175	71	60	468	142	63	57	262	100	113	41	254	169	81	250	1,234
$\text{Ca}(\text{OH})_2$	299	253	71	64	695	176	64	60	300	103	108	42	253	192	65	257	1,505	271	7.6
CaO-MgO^*	267	256	68	53	644	150	61	55	266	120	122	42	284	195	76	271	1,465	231	6.5†‡
CaO-MgO^\dagger	187	279	70	66	602	163	64	57	284	99	105	45	249	188	67	255	1,390	156	4.4‡§

* Calcined dolomite 46.53 per cent CaO , 32.85 per cent MgO —Supplying 1184.8 pounds CaO and 815.2 pounds $\text{CaO} \rightleftharpoons$, respectively.

† Mixtures of CaO and MgO from separately calcined marble and magnesite.

‡ Based on CaO content of high magnesian lime.

§ Based on MgO content of calcined CaO and calcined MgO mixture.

disintegration, and another when there was a persistence of undisintegrated particles (6, p. 323-328; 7, p. 450, 451). Again, the ratio of calcium outgo to magnesium outgo from an incorporation of dolomite in the upper zone will vary decidedly from that obtained from the same incorporation in the lower zone, when the dolomite is of sufficient fineness to insure near-complete disintegration (2). It therefore becomes desirable to determine what relationship obtains for Ca:Mg outgo when calcium and magnesium are added jointly in caustic form and in amounts which are completely, or almost completely, fixed by the surface soil (4) in its upper and lower zones.

In comparing the pulverulent and more active calcium and magnesium materials, it is not permissible to base the comparison solely upon those properties of the alkali-earth materials which are characteristic of them prior to their absorption by the soil. Thorough incorporation of economic additions of caustic forms in a similar loam soil resulted in rapid and practically complete absorption of the base within 10 days (1, 9), under favorable moisture conditions. It is important to remember, therefore, that after a short period—often only a few days—the properties of the absorption complexes become of paramount importance. Those of calcium differ from those of magnesium in their resistance to hydrolysis, and such differences may be reflected in the reactions which take place after economic additions are “fixed” in the soil.

OBJECTIVES

The present contribution is based upon a 4-year study of the influences exerted by three equivalent caustic limes, subsequent to the period of a few days required for their complete absorption. Natural leachings of Calcium, Magnesium, Ca-Mg, nitrates, and sulfates were obtained by means of an outdoor lysimeter equipment in comparing: 1. High-calcic and high-magnesian burnt limes; 2. Burnt dolomite and equivalent mixtures of CaO and MgO, derived from separately calcined marble and magnesite; 3. Surface-zone and subsurface-zone incorporations in their effects upon (1) and (2); 4. Initial and subsequent availability of absorbed calcium and Ca-Mg, as influenced by *diminishing residues* and by *aging*.

EXPERIMENTAL

Two tanks containing a fertile, carbonate-free, brown, acid loam were compared with six tanks containing the same soil and additions of the three caustic limes. These tanks were included in a group previously described and illustrated (3). Plant growth was excluded and the soils were undisrupted during the 4-year period. The soil contained 0.2617 per cent of CaO and 0.3439 per cent of MgO when placed. These total percentages were equivalent to 9340 pounds and 17,072 pounds of CaCO₃, respectively, on the basis of 2,000,000 pounds of moisture-free soil. Each addition was incorporated only in the upper zone, or half, of the surface soil, in comparison

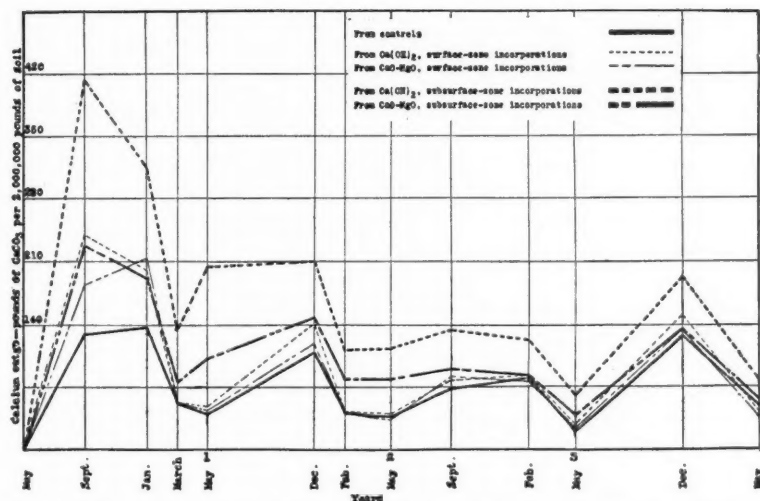


FIG. 1. PROGRESSIVE CALCIUM OUTGO, AS POUNDS OF CaCO_3 -EQUIVALENT PER 2,000,000 POUNDS OF SOIL, FROM CONTROLS, SURFACE-ZONE AND SUBSURFACE-ZONE INCORPORATIONS OF $\text{Ca}(\text{OH})_2$ AND CaO-MgO DURING A 4-YEAR PERIOD

All incorporations at the equivalent rate of 3570 pounds of CaCO_3 (2000 pounds CaO)

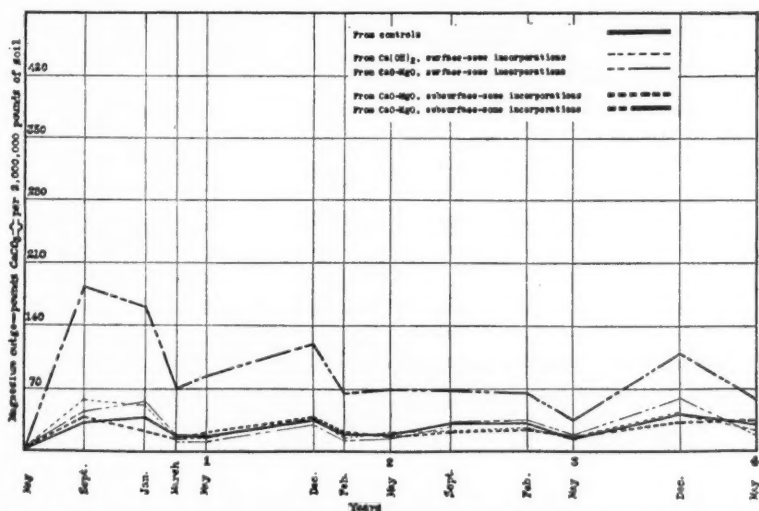


FIG. 2. PROGRESSIVE MAGNESIUM OUTGO, AS POUNDS OF CaCO_3 -EQUIVALENT PER 2,000,000 POUNDS OF SOIL, FROM CONTROLS, SURFACE-ZONE AND SUBSURFACE-ZONE INCORPORATIONS OF $\text{Ca}(\text{OH})_2$ AND CaO-MgO DURING A 4-YEAR PERIOD

All incorporations at the equivalent rate of 3750 pounds of CaCO_3 (2000 pounds CaO)

with the same incorporation in the lower zone without addition to the upper zone. The incorporations were all equivalent to 3570 pounds of CaCO_3 (2000 pounds CaO) per 2,000,000 pounds of soil, moisture-free basis when the full depth, or both zones, are considered. On the same basis, all leachings of calcium, magnesium, and Ca-Mg are expressed as pounds of CaCO_3 . The enhancements in outgo, over the average from the controls, are also expressed as pounds and as per cent of the addition of calcium, magnesium, or Ca-Mg.

The high-calcic lime was practically free of MgO , whereas the two high-magnesian materials contained 46.53 per cent CaO and 32.85 per cent MgO . In each CaO-MgO incorporation an equivalence of 2000 pounds of CaO —3570

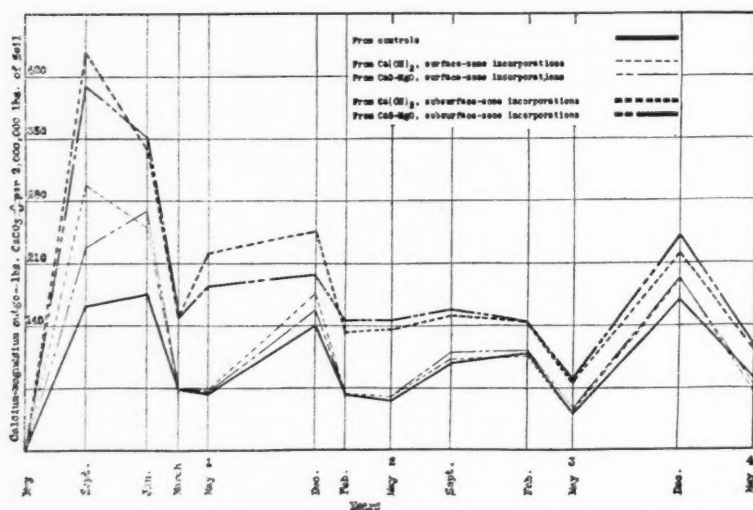


FIG. 3. PROGRESSIVE CALCIUM-MAGNESIUM OUTGO, AS POUNDS OF CaCO_3 -EQUIVALENT PER 2,000,000 POUNDS OF SOIL, FROM CONTROLS, SURFACE-ZONE AND SUBSURFACE-ZONE INCORPORATIONS OF Ca(OH)_2 AND CaO-MgO DURING A 4-YEAR PERIOD

All incorporations at the equivalent rate of 3750 pounds of CaCO_3 (2000 pounds CaO)

pounds of CaCO_3 —was accounted for jointly by 1184.8 pounds and 815.2 pounds for CaO and MgO , respectively. On the basis of chemical equivalence the ratio of CaO:MgO was therefore 1.453 to 1.

DISCUSSION

Calcium, magnesium, and Ca-Mg outgo

Surface-zone incorporations. The outgo of calcium, magnesium and Ca-Mg from controls and from each surface-zone incorporation is given in table 1 and in figures 1, 2, and 3. The leachings from this upper-zone series were

subject, of course, to stoppage by the untreated lower zone. In considering the relationship of Ca:Mg outgo from the several incorporations, it is well to remember that the outgo of calcium from the controls was always greater than that of magnesium. During the first year the Ca:Mg outgo was at the ratio of 3.2:1, and about 2.4:1 as an average during the last 3 years.

The results show maximum outgo from the controls and maximum increase in outgo of both calcium and magnesium from all incorporations during the first year. Thereafter the differences, if any, between controls and treatments were small. The high-calcic lime yielded 102 pounds more of CaCO_3 than the average outgo from the two high magnesian limes for the 4-year period and one-half of this increase was accounted for during the first year. The CaO content of the Ca(OH)_2 was 1.69 times that of the magnesian limes, whereas the total increase in calcium outgo from the hydrated lime was 1.72 times that as an average from the CaO-MgO incorporations.

The magnesium outgo from Ca(OH)_2 was somewhat greater than that from the controls. This was the result of the first year's outgo and may readily be accounted for by assuming that an interchange of calcium for magnesium took place during the first year of maximum generation of nitrates and sulfates, while these salts were passing through the lower zone to which no Ca(OH)_2 was added. The average of the magnesium losses from the two magnesian limes was less than that from Ca(OH)_2 and only 23 pounds in excess of that from the control during the first year. Thereafter it was generally comparable with that from the controls. However, the average enhancement in calcium outgo from the magnesian limes during the first year was 132 pounds as against 186 pounds from the hydrated lime incorporation which carried 1.69 times more calcium. A similar relationship obtains for the 4-year totals, and it is thus apparent that either less magnesium than calcium passed from the upper zone or more magnesium than calcium was stopped by the lower, untreated zone. This point will be considered later in connection with the parallel data from the subsurface-zone incorporations. The maximum acceleration in Ca-Mg outgo came from the Ca(OH)_2 , and amounted to only 7.6 per cent of the addition. The results from the two magnesian limes did not vary greatly, but the outgo from the separately calcined mixture was generally less than that from the equivalent calcined dolomite.

Subsurface-zone incorporations. The results from these incorporations, devoid of any diminishing effect exerted by a lower, untreated zone, are given in table 2 and shown graphically in figures 1, 2, and 3. Disregarding capillary rise of soluble calcium salts from the lower to the upper zone, the rate of treatment in the lower zone might well be regarded as twice that where the full depth of soil is considered. That is, lower-depth incorporations were actually on the basis of 3570 pounds CaCO_3 -equivalence (2000 pounds CaO) per 1,000,000 pounds of soil, since there was no supplementary influence of an underlying zone. The increase in calcium outgo from the Ca(OH)_2 was 707 pounds for the first year, or 60 per cent of that for the 4-year period.

Calcium-magnesium as $\text{CaCO}_3 \approx$

Controls.....	162	175	71	60	468	142	63	57	262	100	113	41	254	169	81	250	1,234
Ca(OH)_2	449	340	149	222	1,160	246	134	136	516	151	144	77	372	221	113	334	2,382	1,148	32.1
CaO-MgO^*	440	348	151	185	1,124	275	141	148	564	170	139	83	392	264	105	369	2,499	1,215	34.0†§
CaO-MgO^\dagger	376	356	149	183	1,064	255	150	144	549	148	150	78	376	215	120	335	2,324	1,090	30.5‡§

* Calcined dolomite 46.53 per cent CaO , 32.85 per cent MgO —Supplying 1184.8 pounds CaO and 815.2 pounds $\text{CaO} \approx$ respectively.

† Mixtures of CaO and MgO from separately calcined marble and magnesite.

‡ Based on CaO content of high magnesian lime.

§ Based on MgO content of calcined CaO and calcined MgO mixture.

There was a decided drop to a 250-pound excess above the controls for the second year, with further progressive diminution in outgo for the third and fourth years. The full increase for the 4-year period was only 33.1 per cent of the addition. The 1183-pound enhancement of CaO outgo from the $\text{Ca}(\text{OH})_2$ incorporations for the 4-year period was 2.98 times the average enhancement

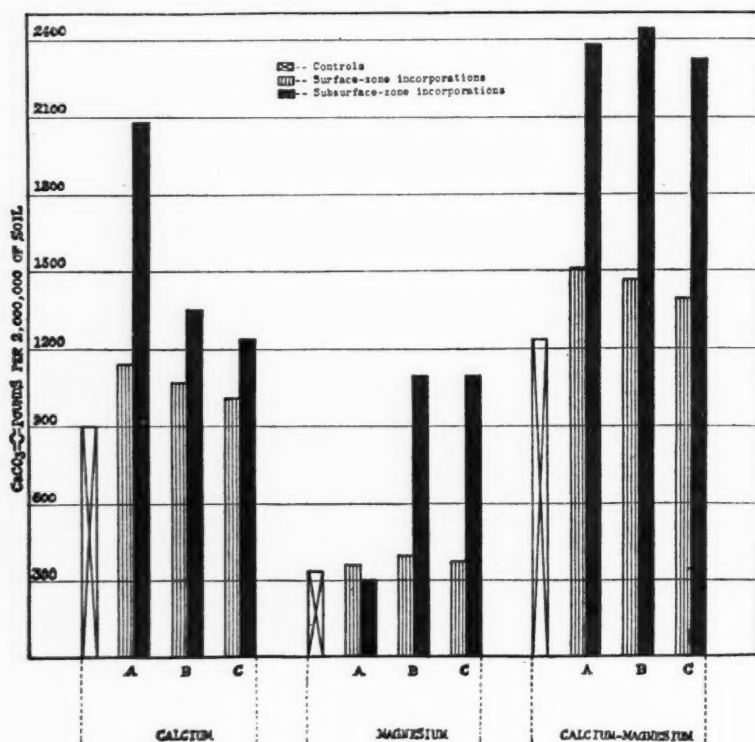


FIG. 4. FOUR-YEAR OUTGO OF CALCIUM, MAGNESIUM, AND Ca-Mg IN TERMS OF CaCO_3 FROM SURFACE-ZONE AND SUBSURFACE-ZONE INCORPORATIONS OF HYDRATED LIME, BURNT DOLOMITE, AND CaO-MgO MIXTURES AT THE RATE OF 3570 POUNDS OF CaCO_3 (2000 POUNDS CaO) PER 2,000,000 POUNDS OF SOIL

A, hydrated lime; B, burnt dolomite; C, separately calcined CaO and MgO

of 397 pounds from the two magnesian limes, although the corresponding ratio of CaO added was approximately 1.69:1. The freshly absorbed non-carbonate complexes furnishes the increase in calcium outgo from the $\text{Ca}(\text{OH})_2$; but, in the case of the CaO-MgO incorporations, the absorbed calcium was not sufficient in amount and distribution to inhibit hydrolysis of some of the absorbed magnesium.

The same order of annual outgo—maximum for the first year, with progressive decrease thereafter—obtains in the calcium results from the two magnesian limes. Each annual outgo of calcium from the separately calcined oxides was less than the corresponding one from the chemically equivalent burned dolomite. It is possible that variations in critical temperatures of calcination may account for these differences.

The magnesium content of the leachings from the high-calcic lime was less than that from the untreated soil during three of the four years, and the 4-year total was less. This indicates a repression of the solubility of native magnesium, in accord with previous observations in parallel studies where there was no opportunity for interference of underlying zones (6, 7). The total magnesium losses from the two types of magnesian lime were in accord, and, in general, those of the several collections and annual period were comparable. Although the average enhancements in outgo of calcium and magnesium from the surface-zone incorporations of the two magnesian limes showed a Ca:Mg ratio of 2.66:1, the lower-zone incorporations gave a Ca:Mg ratio of 1:1.90.

The annual losses of Ca-Mg ran somewhat in parallel, with progressive decrease from the first to the fourth year, the greatest differences occurring between the first and second years. The total enhancements of Ca-Mg outgo were comparable, ranging from 30.5 to 34.0 per cent of the amounts added.

Surface-zone versus subsurface-zone incorporation. The comparisons between outgo of calcium, magnesium and Ca-Mg from the two zones of incorporation are given for annual periods and for the 4-year period in table 3.

The maximum excess of lower-zone outgo over that from a corresponding upper-zone incorporation for any year was the 521-pound increase from $\text{Ca}(\text{OH})_2$ during the first year. This is equivalent to 55 per cent of that for the 4-year period. When corrected for the 357-pound outgo from the control the first-year losses attributable to treatment were 186 pounds and 707 pounds for the upper and lower zones, respectively, which gives from the lower zone an excess equivalent to 14.6 per cent of the full addition. Disparity between losses from the two zones decreased progressively thereafter. The high-magnesian limes showed comparable excess of outgo from the deep incorporations over the surface-zone incorporations for the first two years, with decided diminutions in differences for the last two years. As measured by the actual amounts of lime added, the high-calcic, burnt dolomite, and oxide mixtures show excesses in losses amounting to 26.3, 13.6 and 10.6 per cent, respectively, for the 4-year-period.

The earlier leachings from the treatments in the upper zone were rich in neutral calcium salts, which they carried to the lower zone, where there was no protective effect of any added lime. Magnesium replacement, with increased outgo, was accordingly effected in the untreated lower zone.

The only exception to the greater release of either alkali-earth from the lower-zone incorporations is observed in the repressed outgo of magnesium

TABLE 3
Influence of zone of incorporation of 2000-pound CaO equivalents (3570 pounds CaCO_3) of hydrated lime, burnt dolomite, and CaO-MgO upon outgo of total calcium, magnesium, and calcium-magnesium from a loam soil during annual and 4-year periods—terms of CaCO_3 -equivalence per 2,000,000 pounds of moisture-free soil

TREATMENT	FIRST YEAR						SECOND YEAR						THIRD YEAR						FOURTH YEAR						TOTAL FOR 4-YEAR PERIOD				
	Surface zone incor- poration	Subsurface zone in- corporation	Excess outgo from subsurface incor- poration	Surface zone incor- poration	Subsurface zone in- corporation	Excess outgo from subsurface incor- poration	Surface zone incor- poration	Subsurface zone in- corporation	Excess outgo from subsurface incor- poration	Surface zone incor- poration	Subsurface zone in- corporation	Excess outgo from subsurface incor- poration	Surface zone incor- poration	Subsurface zone in- corporation	Excess outgo from subsurface incor- poration	Surface zone incor- poration	Subsurface zone in- corporation	Excess outgo from subsurface incor- poration	Surface zone incor- poration	Subsurface zone in- corporation	Excess outgo from subsurface incor- poration	Surface zone incor- poration	Subsurface zone in- corporation	Excess outgo from subsurface incor- poration	Surface zone incor- poration	Subsurface zone in- corporation	Excess outgo from subsurface incor- poration	per cent	
Calcium as CaCO ₃ ⇌																													
Ca(OH) ₂	543	1,064	521	220	438	218	188	314	126	190	265	75	1,141	2,081	940	26.3													
CaO-MgO*.....	506	634	128	188	315	127	195	216	21	177	188	11	1,066	1,353	287	13.6†													
CaO-MgO†.....	472	558	86	201	292	91	175	206	31	164	180	16	1,012	1,236	224	10.6‡													
Magnesium as CaCO ₃ ⇌																													
Ca(OH) ₂	152	96	—56	80	78	—2	65	58	—7	67	69	2	364	301	—63													
CaO-MgO*.....	138	490	352	78	249	171	89	176	87	94	181	87	399	1,096	697	47.9§													
CaO-MgO†.....	130	506	376	83	257	174	74	170	96	91	155	64	378	1,088	710	48.8§													
Calcium-magnesium as CaCO ₃ ⇌																													
Ca(OH) ₂	695	1,160	465	300	516	216	253	372	119	257	334	77	1,505	2,382	877	24.5													
CaO-MgO*.....	644	1,124	480	266	564	298	284	392	109	271	369	78	1,465	2,449	984	27.5†													
CaO-MgO†.....	602	1,064	462	284	549	265	249	376	127	255	335	80	1,390	2,324	934	26.1‡													

* Calcinced dolomite, 46.53 per cent CaO , 32.85 per cent MgO —Supplying 1184.8 pounds CaO and 815.2 pounds $\text{CaO} \rightleftharpoons$, respectively.

† Mixtures of CaO and MgO from separately calcined marble and magnesite.

‡ Based on CaO content of high magnesic lime.

§ Based on MgO content of calcined CaO and calcined MgO mixture.

from the high-calcic lime incorporations. This may be readily accounted for by "reciprocal repression" (7). The leachings from the untreated zone lying above the lower-zone $\text{Ca}(\text{OH})_2$ incorporations should be comparable to those from the same zone in the tanks which received no additions to either zone. Hence, a repressive, or protective, effect upon the native magnesium of the lower zone was exerted by the deep incorporations of the high-calcic lime, the leachings from which passed directly from the tanks. This is in complete harmony with previous findings (5; 7, p. 450, 451) upon the same soil type, wherein it was shown that an absorbed excess of one alkali-earth may force back, or even inhibit, the tendency of its soluble neutral salts to effect interchange of the other alkali-earth.

The total excess of subsurface-zone magnesium outgo over that from the surface-zone incorporations was practically the same for the two magnesian limes. The magnesium excesses from the lower-zone additions of magnesium lime showed the same order—maximum for the first year and subsequent decreases—as that obtained in the calcium outgo from the high-calcic lime. It was shown (table 3) that the leachings from the surface-zone incorporations of CaO-MgO carried more calcium than magnesium, and it was stated that this was due to either lesser outgo of magnesium from the upper zone or greater magnesium absorption from the upper-zone leachings during their passage through the lower zone. In view of the greater outgo of magnesium from the same CaO-MgO incorporations in the lower zone, the latter explanation would seem to be more tenable.

The Ca-Mg totals from the three limes did not differ greatly in annual and 4-year intrazone comparisons. There was a consistent decrease in the disparity between greater outgo from the lower-zone and lesser outgo from the upper-zone incorporations after the first year, and in proportions greater than those to be anticipated from progressive decrease of residuals. The ratio of the group-average disparity in outgo for the first year to that for the second year was 2.57:1, whereas that for the second to third was 2.25:1, and that for the third to fourth 1.51:1, as accounting for the average increase in total outgo, which amounted to 26 per cent of the Ca-Mg added.

Nitrate and sulfate outgo

Surface-zone incorporations. The nitrate and sulfate leachings from surface-zone incorporations are given in table 4, as pounds of nitrogen and sulfur per 2,000,000 pounds of soil. At the beginning of the experiment the soil contained 0.1050 per cent, or 2100 pounds of nitrogen and 0.057 per cent, or 1140 pounds of sulfur on the same basis. The average annual increment of sulfur over a period of 9 years prior to the present experiment was 51.5 pounds (8), whereas that calculated from concomitant rain water was 180.4 pounds, or 45.1 pounds per annum.

The acceleration of nitrate outgo from the surface-zone incorporations of each of the three limes is attributable mainly to the increases during the first

TABLE 4
Nitrate nitrogen and sulfate sulfur leached during 4 years from 2000-pound CaO equivalents (3570 pounds CaCO_3) of hydrated lime, burnt dolomite and mixtures of separately calcined CaO and MgO incorporated in the surface zone of a loam soil—basis of 2,000,000 pounds moisture-free soil

TREATMENTS	FIRST YEAR						SECOND YEAR						THIRD YEAR						FOURTH YEAR				TOTAL FOR 4-YEAR PERIOD	4-YEAR INCREASE OVER CONTROLS
	May to September	September to January	January to March	March to May	Total	lbs.	May to December	December to February	February to May	Total	lbs.	May to September	September to February	February to May	Total	lbs.	May to December	December to May	May to December	December to May	Total	lbs.		
	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.		
Controls.....	20.8	32.1	3.3	6.9	63.1	32.4	32.4	2.3	2.4	37.1	21.1	11.2	1.8	34.1	29.6	5.1	34.7	169.0
$\text{Ca}(\text{OH})_2$	28.9	47.6	4.9	6.7	88.1	41.7	3.5	1.6	46.8	20.9	4.1	3.3	28.3	29.6	2.3	31.9	195.1	26.1	26.1	26.1	26.1	26.1	26.1	26.1
CaO-MgO^*	34.8	37.6	3.9	2.5	78.1	37.9	1.8	1.0	40.7	25.2	9.9	3.2	38.3	26.9	2.7	29.6	186.7	17.7	17.7	17.7	17.7	17.7	17.7	17.7
CaO-MgO^\dagger	39.1	45.7	4.4	3.9	93.1	39.2	2.8	1.4	43.4	20.0	5.7	3.2	28.9	26.5	2.4	28.9	194.3	25.3	25.3	25.3	25.3	25.3	25.3	25.3
Sulfate sulfur																								
Controls.....	9.5	16.7	17.6	8.1	51.9	11.4	11.8	9.3	32.5	4.8	12.0	8.5	25.3	9.4	16.0	25.4	135.1
$\text{Ca}(\text{OH})_2$	15.4	29.2	14.7	7.9	67.2	13.8	9.3	8.2	31.3	4.1	16.9	6.1	27.1	14.6	15.6	30.2	155.8	20.7	20.7	20.7	20.7	20.7	20.7	20.7
CaO-MgO^*	11.8	29.0	16.3	9.6	66.7	12.7	9.1	8.5	30.3	4.7	16.5	5.5	26.7	12.9	16.3	29.2	152.9	17.8	17.8	17.8	17.8	17.8	17.8	17.8
CaO-MgO^\dagger	5.4	29.6	16.3	9.5	60.8	13.2	9.8	9.3	32.3	4.7	15.9	6.0	26.6	15.1	15.5	30.6	150.3	15.2	15.2	15.2	15.2	15.2	15.2	15.2

* Calcined dolomite 46.53 per cent CaO 32.85 per cent MgO—Supplying 1184.8 pounds CaO and 815.2 pounds CaO ∞ , respectively.

† Mixtures of CaO and MgO from separately calcined marble and magnesite.

TABLE 5

Nitrate nitrogen and sulfate sulfur leached during 4 years from 2000-pound CaO-equivalences (3570 pounds CaCO_3) of hydrated lime, burnt dolomite, and mixtures of separately calcined CaO and MgO incorporated in the subsurface zone of a loam soil—basis of 2,000,000 pounds moisture-free soil

TREATMENT	FIRST YEAR						SECOND YEAR						THIRD YEAR						FOURTH YEAR				TOTAL FOR 4-YEAR PERIOD	4-YEAR INCREASE OVER CONTROLS
	May to September	September to January	January to March	March to May	May to September	Total	May to December	December to February	February to May	May to September	Total	May to December	December to February	February to May	May to September	Total	May to December	December to February	February to May	May to September	Total	Total		
	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.
Nitrate nitrogen																								
Controls.....	20.8	32.1	3.3	6.9	63.1	32.4	2.3	2.4	37.1	21.1	11.2	1.8	34.1	29.6	5.1	34.7	169.0
Ca(OH) ₂	38.9	35.7	3.6	6.4	84.6	26.7	1.4	0.8	28.9	24.9	3.1	3.2	31.2	26.6	2.3	28.9	173.6	4.6	4.6	4.6	4.6	4.6	4.6	4.6
CaO-MgO*.....	35.0	42.0	3.8	3.3	84.1	34.9	1.4	0.8	37.1	24.9	5.2	3.4	33.5	29.9	2.4	32.3	187.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0
CaO-MgO†.....	31.9	44.7	4.0	4.7	85.3	33.2	0.7	0.6	34.6	18.7	4.9	2.6	26.2	27.3	4.0	31.3	177.4	8.4	8.4	8.4	8.4	8.4	8.4	8.4
Sulfate sulfur																								
Controls.....	9.5	16.7	17.6	8.1	51.9	11.4	11.8	9.3	32.5	4.8	12.0	8.5	25.3	9.4	16.0	25.4	135.1
Ca(OH) ₂	28.9	22.8	9.6	5.9	67.2	13.2	7.8	6.1	27.1	5.7	12.7	6.7	25.1	12.6	16.5	29.1	148.5	13.4	13.4	13.4	13.4	13.4	13.4	13.4
CaO-MgO*.....	29.1	24.5	10.7	5.4	69.7	14.0	7.6	7.7	29.3	6.6	12.6	6.6	25.8	12.7	14.9	27.6	152.4	17.3	17.3	17.3	17.3	17.3	17.3	17.3
CaO-MgO†.....	21.7	25.0	10.5	6.3	63.5	14.1	8.0	7.9	30.0	5.7	13.6	6.4	25.7	11.7	16.5	28.2	147.4	12.3	12.3	12.3	12.3	12.3	12.3	12.3

* Calcined dolomite 46.53 per cent CaO, 32.85 per cent MgO—Supplying 1184.8 pounds CaO and 815.2 pounds CaO ∞ respectively.

† Mixtures of CaO and MgO from separately calcined marble and magnesite.

year. After that period the incorporations gave nitrate losses comparable to, and even less than, the outgo from the control, especially during the third and fourth years. The variations between nitrate leaching from the three limes by years need not be stressed, since the maximum increase over the control amounts to only 26.1 pounds for the full 4-year period.

The records of sulfate outgo show the same initial acceleration shown in the case of nitrates during the first year. Only during this year did the sulfate leachings exceed the sulfate content of the rainfall. The concordance for the succeeding three years is very consistent, so that the maximum increase in sulfate leachings from each lime for the 4-year period is very close to that of the first year.

Subsurface-zone incorporations. The leachings from these incorporations are given in table 5. Comparable accelerations of nitrate outgo from subsurface-zone incorporations of the three limes were evidenced during the first year, but not thereafter; and when considered on the basis of average annual accelerations the maximum for any of the treatments was only 4.5 pounds. Acceleration in outgo as a result of mixing and aeration—and that due to this factor, plus treatment—was therefore most noticeable during the first year.

The largest sulfate outgo from the control and that from each of the three limes also came during the first year. The sulfate outgo from the controls equalled rainfall increment only during this year and only then did the three limes yield an amount in excess of that carried by rain waters. Thereafter the controls and the three caustic limes gave results so close that the respective 4-year totals were practically the same as their corresponding increases for the first year.

Surface-zone versus subsurface-zone incorporations

The variations between nitrate and sulfate losses from the two zones are given in table 6. Only in the case of the hydrated high-calcic lime was there an appreciable difference in the outgo of nitrate nitrogen from the two zones during the 4-year period. The plus and minus variations—with a maximum of 16.9 pounds, as a total for subsurface-zone over surface-zone incorporations—show that no extensive differences resulted from variation in depth of incorporation.

The sulfate differences were small, varying from plus to minus, and the differences between the totals for the 4-year period were insignificant. The average yield of total sulfur from the controls was, however, 45.4 pounds per acre less than that carried by rain water during the 4-year period. The average enhancement for all treatments in both zones was 16.1 pounds. Consequently, even with this enhancement in outgo, all sulfate leachings were uniformly less than the sulfate increment through rainfall.

From the foregoing it appears that the previously discussed differences in outgo of Ca-Mg were not to be accounted for by any material variation in

TABLE 6

Influence of zone of incorporation of 2000-pound CaO equivalents 3570) pounds CaCO₃) of hydrated lime, burnt dolomite, and CaO-MgO upon culgo of nitrate nitrogen and sulfate sulfur from a loam soil during annual and 4-year periods—basis of 2,000,000 pounds of moisture-free soil

TREATMENT	FIRST YEAR			SECOND YEAR			THIRD YEAR			FOURTH YEAR			TOTAL FOR 4-YEAR PERIOD		
	Surface zone incor-	Subsurface zone in-	Surface zone rela-	Surface zone incor-	Subsurface zone in-	Surface zone rela-	Surface zone incor-	Subsurface zone in-	Surface zone rela-	Surface zone incor-	Subsurface zone in-	Surface zone rela-	Surface zone incor-	Subsurface zone in-	Surface zone rela-
	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.
Nitrate nitrogen															
Ca(OH) ₂	88.1	84.6	+3.5	46.8	28.9	+17.9	28.3	31.2	-2.9	31.9	28.9	+3.0	195.1	173.6	+21.5
CaO-MgO*.....	78.1	84.1	-6.0	40.7	37.1	+3.6	38.3	33.5	+4.8	29.6	32.3	-2.7	186.7	187.0	+0.3
CaO-MgO†.....	93.1	85.3	+7.8	43.4	34.6	+8.8	28.9	26.2	+2.7	28.9	31.3	-2.4	194.3	177.4	+16.9
Sulfate sulfur															
Ca(OH) ₂	67.2	67.2	Equal.	31.3	27.1	+4.2	27.1	25.1	+2.0	30.2	29.1	-1.1	155.8	148.5	+7.3
CaO-MgO*.....	66.7	69.7	-3.0	30.3	29.3	+1.0	26.7	25.8	+0.9	29.2	27.6	-1.6	152.9	152.4	+0.5
CaO-MgO†.....	60.8	63.5	-2.7	32.3	30.0	+2.3	26.6	25.7	+0.9	30.6	28.2	-2.4	150.3	147.4	+2.9

* Calcined dolomite 46.53 per cent CaO, 32.85 per cent MgO—Supplying 1184.8 pounds CaO and 815.2 pounds CaO ∞ , respectively.

† Mixtures of CaO and MgO from separately calcined marble and magnesite.

amounts of biological end-products. Rather, they were due primarily to greater hydrolysis of absorption complexes and greater leaching of the resultant bicarbonates of the two elements from the incorporations in the more moist lower zone.

Diminishing availability of absorbed calcium and Ca-Mg

The relationship between each total outgo and that for the first year and that of each succeeding year emphasized the point advanced (7, p. 461) in a related study with the same type of soil, where incorporations were made throughout the entire soil mass; namely, that the absorbed alkali-earths appear to resist hydrolysis more and more as they age. Earlier related studies showed that the calcium hydroxide additions must have been absorbed—directly from the hydroxide or after a part of the hydroxide had reverted to

TABLE 7

Influence of diminishment of residuals and of aging upon the availability of absorbed calcium from $\text{Ca}(\text{OH})_2$ and absorbed Ca-Mg from CaO-MgO incorporations at the constant rate of 2000 pounds of CaO (3570 pounds CaCO_3) per 1,000,000 pounds of subsurface-zone loam, as measured by Ca and Ca-Mg outgo, respectively—terms of pounds CaCO_3

LEACHING PERIOD	CALCIUM FROM $\text{Ca}(\text{OH})_2$ INCORPORATIONS				Ca-Mg FROM CaO-MgO INCORPORATIONS*			
	Present at beginning of period	Leached during period†	Outgo as related to residue of incorporation		Present at beginning of period	Leached during period†	Outgo as related to residue of incorporation	
			ratio	per cent			ratio	per cent
First year.....	3,570	707	1: 5.05	19.80	3,570	626	1: 5.70	17.53
Second year.....	2,863	250	1:11.45	8.73	2,944	295	1: 9.98	10.02
Third year.....	2,613	137	1:19.07	5.24	2,649	130	1:20.38	4.91
Fourth year.....	2,476	89	1:27.82	3.59	2,519	102	1:24.70	4.05

* Average of burnt dolomite and separately calcined CaO and MgO.

† In excess of outgo from controls.

the carbonate—within a period of 10 days (1), and that at the close of the present experiment only small and near-equal amounts of carbonates remained (3, p. 410) from the $\text{Ca}(\text{OH})_2$ and CaO-MgO incorporations. It is evident that, if a study of influence of time upon availability is desired, it is essential that no untreated zone be interposed between the zone of treatment and the outlets for the leachings. This precludes the use of the upper-zone series in this connection. The series which received the $\text{Ca}(\text{OH})_2$ and CaO-MgO in the lower zone may, however, be utilized for this purpose.

Table 7 shows the excess of calcium lost from the lower-zone incorporation of $\text{Ca}(\text{OH})_2$ over the calcium outgo from the controls, and the average excess of Ca-Mg from the deep incorporations of the two types of magnesian lime. It also shows the fractions of the incorporations present at the beginning of each annual period, and the ratio and percentage relationships of such to each

annual enhancement in outgo. Table 2 shows that the amounts of calcium and magnesium lost from the controls were greatest during the first year, with near-constant outgo thereafter. It also shows that the maximum outgo of calcium from $\text{Ca}(\text{OH})_2$ and Ca-Mg from the CaO-MgO incorporations was greatest during the first year, with a marked decrease during the second year and further decreases during the succeeding two years. The maximum outgo of nitrates and sulfates during the first year fails to account for the loss of calcium and magnesium, and it follows that acceleration of CO_2 -production occurred in parallel with the production of the nitrates and sulfates. This has been established also by determinations of the bicarbonate content of the leachings. If this parallel of accelerated nitrate, sulfate, and CO_2 production had continued during the last three years, sufficient H_2CO_3 would have been available to maintain a bicarbonate outgo with a uniformity akin to that shown by the nitrate and sulfate leachings of table 5. But no such parallel in maintenance of outgo obtained. The losses of calcium from the $\text{Ca}(\text{OH})_2$ incorporations and the losses of Ca-Mg from the CaO-MgO incorporations suffered a decided decrease from year to year.

The ratios of calcium outgo to calcium addition, or its residual fraction, increased progressively from 1:5.05 for the first year to 1:27.82 for the fourth year, with conversely decreasing percentage extremes of 19.80 and 3.59. Similar extreme ratio values of 1:5.70 and 1:24.70 and percentage converse extremes of 17.53 and 4.05 obtain in expressing enhancements in Ca-Mg outgo as related to added CaO-MgO. The amount of calcium added as $\text{Ca}(\text{OH})_2$ —all but a small amount of which was quickly absorbed in non-carbonate combination—was 1.44 times that fraction which remained at the beginning of the fourth year; but the amount of calcium leaching during the first year was 7.85 times that leached during the fourth year. Or, at the beginning of the fourth year, the residue from the $\text{Ca}(\text{OH})_2$ incorporation was 69.4 per cent, whereas the enhancement in calcium leaching during the fourth year was only 12.6 per cent of that during the first year. The enhancement in outgo of Ca-Mg from the CaO-MgO incorporations shows the same general relationship between additions and annual residuals as those pointed out for calcium outgo and additions.

If the organic matter washed down by rain and that possibly derived from algae be disregarded, the only organic matter available for the generation of bacterial end-products during the experiment was the well-humified material present when the soil was placed. If the disintegration of this organic matter was at its maximum during the first year, and if thereafter it continued at the rate indicated by nitrate and sulfate outgo, diminishing residuals and their decreasing solubility would be the dominant causal factors in the progressive decrease in alkali-earth outgo during the last three years. But, if the amounts of CO_2 available to effect bicarbonate solutions of the hydrolyzed Ca-Mg decreased steadily, then the outgo of the two elements would have decreased, irrespective of the other two factors.

Expressed on the basis of full depth of surface soil, the initial CaCO_3 -equivalent of the non-carbonate calcium content of 9340 pounds was supplemented by 3570 pounds from the lower-zone incorporation of Ca(OH)_2 at the beginning of the present experiment. The total uncorrected outgo from this augmented supply of 12910 pounds during the first year was 1064 pounds, or 8.24 per cent. Deducting from the initial supply of 12910 pounds the sum of the first year's outgo and the decreasing losses of 438 pounds and 314 pounds for the second and third years—i.e., 1816 pounds—there remained 11094 pounds at the beginning of the fourth year. If the same relation between total calcium content and outgo which obtained for the first year had continued throughout the first three years, the amount of calcium-carbonate-equivalent leached during the fourth year would have been 824 pounds, but the amount which did leach during the fourth year was only 265 pounds, or 2.66 per cent, of that present at the beginning of the fourth year. By using the surface-zone incorporation of Ca(OH)_2 for the same method of calculation, the outgo for the first year was found to be 4.21 per cent of that present, whereas that for the fourth year was only 1.59 per cent. The outgo from the controls for the four years were, in order, 3.82, 2.09, 2.01, and 2.04 per cent of the amount present at the beginning of each of the respective years. Corresponding values of 8.24, 3.70, 2.75, and 2.39 per cent express the proportions of the four annual losses of calcium from that originally present plus the unleached fraction of the subsurface-zone incorporation of Ca(OH)_2 present at the beginning of the respective years. If, however, the initial year of maximum outgo of all components be disregarded, and the 3.70 per cent of calcium outgo for the second year be applied to the residuals present at the beginning of the third and fourth years, on the assumption of uniform proportions between outgo and residues, the calculated values of 422 pounds and 410 pounds for the third and fourth years, respectively, are obtained. But the corresponding amounts actually leached were only 314 pounds and 265 pounds. These findings, together with the decrease of about one-half in outgo of calcium, magnesium, and Ca-Mg during the second year, and the approximation of the nitrate and sulfate outgo to that of the controls during the second, third, and fourth years, for both zones in all cases, indicate that enhanced outgo was accounted for in the main by biological accelerations only during the first year. In the absence of marked bacterial activities after that period, it appears that decreasing solubility—i.e., decreased hydrolysis—of the thoroughly disseminated absorption complexes was responsible for steadily decreasing outgo of alkali-earths. The combined Ca-Mg from the CaO-MgO incorporations develop corresponding relationships.

It is generally held that a second liming is required to maintain any benefits obtained from the initial application of the usual 2000-pound CaO-equivalent treatment, and it is usually thought that such reliming should be made after a period of from four to six years. It has been assumed that the need of

repetition was due to the loss of added lime through leaching and to its assimilation by plants. Such an assumption predicates that the absorption complexes derived from added lime are decidedly more soluble than those native to the soil. It is equally permissible to assume that the absorbed lime acquires in time the properties possessed by the native non-carbonate inorganic calcium compounds of the soil. From the foregoing it appears reasonable to assume that under the dynamic conditions prevalent in the soil system there is a tendency for the absorbed alkali-earths to become more and more insoluble, possibly more and more complex in make-up, and approaching in character the aged non-carbonate materials native to the soil. Under humid conditions this would obtain in greatest degree with a soil of the "heavier" type, containing materials sufficiently fine and acid to be designated as "acidoids" (10), the neutralization of which results in the fixation of added alkali-earths. With a soil having a minimum of such finely divided material, the fixation would not be extensive, greater leaching would occur, and additional lime would be needed to care for the paucity of alkali-earth nutrients. With a loam of the type used in this experiment, reliming in practice would probably be required to insure optimum reaction for biological activation and ready supplies of nutrients long before the removal of even a major part of the added lime; that is, most of the first addition of lime would still be present, but a second application would be beneficial. It appears most probable, therefore, that the function of such a supplemental supply of lime would be to furnish a "fresh stream" of alkali-earth of greater availability than that which had been previously absorbed, in order to offset progressive decrease in solubility, rather than the absolute supplementing of the total supplies of earthy materials and the replenishment of losses caused by leaching.

SUMMARY

Results are given from a 4-year lysimeter study of outgo of calcium, magnesium, Ca-Mg, nitrates, and sulfates from surface-zone and subsurface-zone incorporations of Ca(OH)_2 , burnt dolomite, and a corresponding CaO-MgO mixture, at a constant rate of 3570 pounds of CaCO_3 (2000 pounds of CaO) per 2,000,000 pounds of loam soil, moisture-free basis, as a result of an average annual rainfall of 51 inches.

The outgo of calcium from each lime was greatest during the first year, with progressive decrease thereafter, for both zones of incorporation. Because of a decidedly greater outgo from the subsurface-zone incorporation of Ca(OH)_2 , the conservation of lime exerted by the full soil depth upon the upper-zone incorporations was 940 pounds, or 26.3 per cent of the addition.

The magnesium outgo from the surface-zone incorporations of CaO-MgO was augmented during the first year, although practically the same as that from the controls during the succeeding three years; whereas it was enhanced

in all four annual leachings from the subsurface-zone incorporations, the maximum having been obtained during the first year.

The 4-year aggregates of Ca-Mg from the surface-zone incorporations of the three limes were comparable for each year and for the 4-year period. The totals of Ca-Mg from the subsurface-zone incorporations of the three limes were also comparable by yearly comparisons, with maximum for the first year and decreases thereafter. Each annual outgo, and that for the full period, was about 5 times as great as the corresponding one from incorporations in the upper zone.

Slight interchange of calcium for magnesium was found when the excess of calcium salts from the treated surface zone passed to the untreated lower zone, whereas "reciprocal repression" was noted in the direct leachings from the excess of absorbed calcium in the lower zone.

In general, accelerations in nitrate and sulfate outgo from CaO and CaO-MgO were appreciable and comparable during the first year. However, there was no marked variation thereafter, so that the respective increases for the 4-year period were uniformly about the same as the corresponding ones for the first annual period. Except during the first year, the nitrate and leachings were small during the winter months in all cases. No marked differences obtained as a result of difference in the zone of incorporation. Even with acceleration in sulfate outgo, the amount leached was, in no case, equivalent to the increment from rain water for the 4-year period.

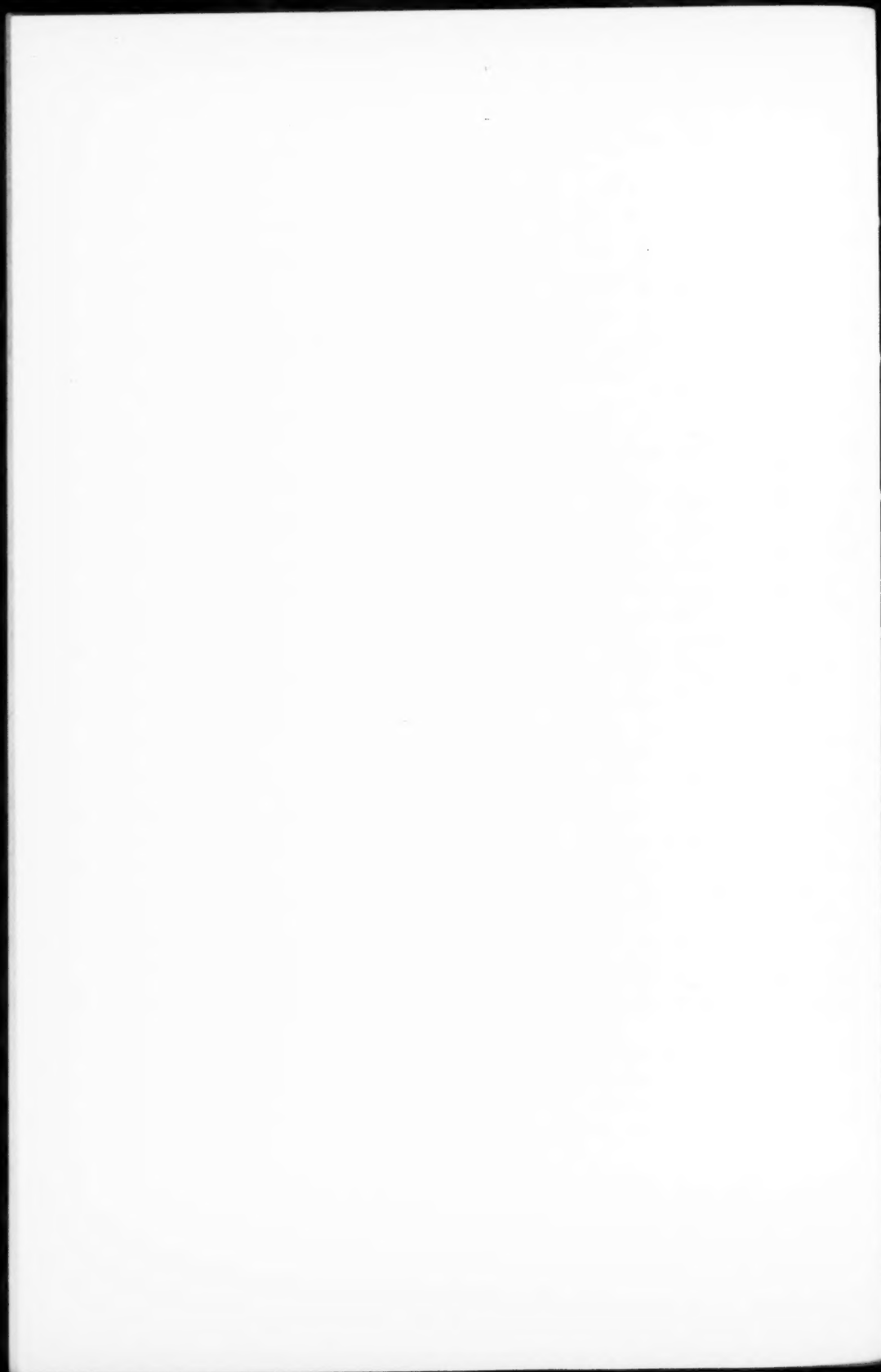
The Ca-Mg proportion in the leachings from CaO-MgO varied with the zone of incorporation. Upper-zone leachings carried about twice as much calcium as magnesium, whereas the lower-zone incorporations yielded about twice as much magnesium as calcium. (These relationships correspond to those which obtained when finely ground dolomite was incorporated in the two zones of the same soil.)

With this particular soil and rate of incorporation, the principal differences resulting from equivalent incorporations of Ca(OH)_2 and CaO-MgO were (a) variations in the proportion of calcium to magnesium in the leachings; (b) more extensive leachings of calcium and more extensive fixation of magnesium by the lower zone from equivalent quantities of calcium and magnesium; (c) Ca:Mg proportions of 1.7 to 1 in outgo from the upper-zone incorporation and 3 to 1 from the incorporations in the lower zone; and (d) somewhat greater calcium and Ca-Mg outgo from the burnt dolomite than from the corresponding separately calcined CaO-MgO, for both zones.

The progressive decrease in outgo of calcium and Ca-Mg is apparently not due so much to diminished residuals as to the diminishing solubility of such residuals, so that repetition of liming may become necessary, not primarily to offset outgo, but rather because of the need of more newly absorbed and more soluble non-carbonate forms, or undisintegrated carbonate residuals.

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POTASSIUM CONTENT OF PLANTS AS AN INDICATOR OF AVAILABLE SUPPLY IN SOIL

J. W. AMES AND R. W. GERDEL

Ohio Agricultural Experiment Station

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Numerous investigations on the ash constituents of plants have been made from time to time in order to obtain information concerning available soil nutrients. Although the ash of certain plants has been found to vary with the soil in which they were grown, there are so many factors involved that the method may not furnish more reliable results than can be secured from a chemical analysis of the soil.

One of the more recent procedures proposed for using the plant as an analytical agent is the method described by Neubauer and Schneider (2), in which a large number of plants are grown for a limited time in a small amount of soil. The authors state that the method is based on the fact that seedlings do not live as long as possible upon the reserve materials of the seeds, but obtain nutritive substances from the soil through their rootlets as soon as they are developed.

It is considered that if a large number of young seedlings are grown in a small quantity of soil, the starving rootlets extract all the assimilable nutritive substances their strength permits, and thus separate the available from the non-available plant nutrients.

The details of the seedling method devised by Neubauer for ascertaining the fertilizer requirements of soils are essentially as follows:

In the bottom of a small glass dish having a diameter of approximately 11 cm. and a depth of 7 cm., is placed 100 gm. of carefully prepared soil, mixed with 50 gm. of pure sand. Over this soil and sand mixture the greater portion of 250 gm. of sand is spread, a sufficient amount for a $\frac{1}{2}$ -cm. covering over the seeds being reserved. A small glass tube for aeration and watering is placed in the center of the dish. After the dishes are prepared 100 carefully selected rye seeds are planted, water is added and the weight of the dishes obtained.

Neubauer states that the seed should weigh about 40 gm. to the one thousand, and be treated with a chlorphenol-mercury compound, "Upsulun." A kilogram of seed is treated for about 1½ hours with a liter of a 0.1 per cent Uspulun solution containing 0.3 gm. sodium hydroxide, then dried on blotting paper and allowed to remain exposed to the air for a week. The seeds are germinated by keeping the dish in a moist warm place. After 17 days the seedlings with their rootlets are removed from the soil and sand, and the phosphorus and potassium contents determined.

Considerable attention has been given to the method in various publications, with special reference to its value for determining the fertilizer requirements

of sugar beets. Roemer (3) subjected a large number of soil samples to the Neubauer test in order to determine the ability of soils to satisfy the potassium and phosphate requirement of cultivated crops. The preliminary results of his investigation appear to be in accord with the claims of Neubauer.

In order to ascertain whether this method, or some modification of it embodying the essential features of nutrients utilized by plants, has possibilities for furnishing indications of supply or deficiency of available potassium in soils, experiments closely allied to this phase of the field of plant nutrition were undertaken.

EXPERIMENTAL

The soils used in this work were chiefly from several fertility experiment plots that have been fertilized and under observation for a period of years. Some of these soils had previously been studied to determine the effect of treatment and cropping on the solubility of potassium.

Several series of tests were made at different times, the proportions of soil and sand, the number of plants, and other conditions being varied somewhat.

In the first series rye was planted and the method of procedure followed was essentially the same as outlined by Neubauer, except that treatment of rye seed with chlorphenol-mercury solution was omitted. This resulted in unsatisfactory germination of the rye. Consequently the number of plants on different soils varied to such an extent that it was not considered worth while to analyze the plants from more than a few of the pots that produced a rather uniform number. Three portions of some of the 15 soils were used, and five or more of others, making a total of 57 pots.

The data for tops and roots weighed and analyzed separately, show that the ratio of tops to roots and the potassium removed by each vary appreciably. On account of the lesser weight and the greater bulk of the muck soil, 50-gm. portions of muck were mixed with sand and planted with 50 seeds. A calculation of the potassium removed from the muck soil on the same basis as from the mineral soils, indicates that it has no less available potassium. The data for this first series are given in table 1. The few results obtained from rye plants in this first experimental work with the method are of no special significance except that they emphasize the necessity of seed treatment to insure a uniform stand of plants.

Comparison of wheat and rye

On account of the unsatisfactory growth of rye in the first test, a comparison of wheat and rye was made by growing plants for 17 days in the same amounts of soil and sand, as recommended by Neubauer except that 80 seeds instead of 100 were planted. The seeds were treated with chlorphenol-mercury compound before planting.

The data in table 2 show that wheat produced larger weights of plants containing increased amounts of potassium. The weights of potassium in

roots of wheat plants in the two soils were also larger, but there was no consistent variation in roots of wheat and rye grown in pure sand. The greater

TABLE 1
Rye plants of first series; grown for 14 days

SOIL	NUMBER OF PLANTS	WEIGHTS OF DRY		POTASSIUM REMOVED BY		POTASSIUM CONCENTRATION	
		Tops	Roots	Tops	Roots	Tops	Roots
		gm.	gm.	mgm.	mgm.	per cent	per cent
Forestry plot.	60	0.609	1.089	12.3	6.3	2.00	0.59
	62	0.520	1.212	11.4	6.2	2.16	0.52
	62	0.529	1.222	12.2	6.9	2.31	0.57
Paulding.	96	0.837	1.434	16.1	8.0	1.92	0.56
	95	0.839	1.089	14.1	10.4	1.69	0.96
Muck.	84	0.790	0.942	9.8	6.4	1.24	0.69
	94	0.840	1.080	11.2	6.4	1.33	0.59
	80	0.822	0.978	11.2	4.6	1.38	0.48
Sand.	91	0.652	1.180	11.0	7.4	1.54	0.63
	88	0.598	1.114	10.2	6.7	1.71	0.59
	91	0.606	1.138	7.7	7.3	1.27	0.64

TABLE 2
Comparison of wheat and rye

SOIL	CROP	NUMBER OF PLANTS	WEIGHT OF TOPS	WEIGHT OF ROOTS	POTASSIUM IN		POTASSIUM CONCENTRATION	
					Tops	Roots	Tops	Roots
			gm.	gm.	mgm.	mgm.	per cent	per cent
Pure sand.	Rye	79	0.5871	1.1452	5.2	5.1	0.889	0.443
	Rye	74	0.5500	0.7955	4.5	4.2	0.818	0.522
	Wheat	80	0.8177	1.2716	7.5	5.7	0.915	0.349
	Wheat	80	0.8057	1.2542	6.6	5.1	0.818	0.404
Silt loam.	Rye	70	0.5477	0.6018	7.2	3.0	1.321	0.506
	Rye	73	0.6027	0.7077	7.1	3.7	1.173	0.518
	Wheat	80	0.8373	1.1388	9.7	6.2	1.162	0.545
	Wheat	74	0.7745	1.1247	10.7	6.6	1.380	0.589
Clyde sand.	Rye	72	0.7276	0.9045	21.0	5.4	2.884	0.595
	Rye	80	0.7268	0.8694	24.0	7.0	3.363	0.809
	Wheat	73	1.0000	1.3127	24.0	9.2	2.429	0.920
	Wheat	80	1.0300	1.4364	27.0	9.0	2.623	0.875

weights of plants grown in the Clyde sandy soil indicate that conditions for growth were more favorable than in the silt loam soil taken from a nitrogen-

and phosphorus-fertilized plot of a 3-year rotation fertility experiment field on the Wooster farm. The potassium content of plants grown in Clyde sand was appreciably greater than that of plants grown in silt loam soil, although

TABLE 3
Potassium removed from several soils by wheat plants

SOIL AND TREATMENT	DRY WEIGHT		POTASSIUM IN			POTASSIUM CONCENTRATION		
	Tops	Roots	Tops	Roots	Entire plant	Tops	Roots	Entire plant
	gm.	gm.	mgm.	mgm.	mgm.	per cent	per cent	per cent
Wooster silt loam;* no treatment.....	0.934	0.934	10.4	4.8	15.2	1.112	0.51	0.814
Wooster silt loam; limed.....	0.823	0.882	9.4	5.1	14.5	1.141	0.58	0.851
Wooster silt loam; acid phosphate fertilizer.....	0.919	0.885	10.7	4.7	15.4	1.163	0.53	0.855
Wooster silt loam; acid phosphate fertilizer; limed.....	0.910	0.988	9.4	6.0	15.4	1.030	0.59	0.809
Wooster silt loam; muriate potash fertilizer.....	0.999	0.817	15.0	5.4	20.4	1.520	0.66	1.130
Forestry soil.....	1.040	0.859	29.7	6.0	35.7	2.840	0.73	1.882
Clyde clay.....	0.962	0.869	18.8	7.0	25.8	1.941	0.82	1.383
Clyde sand.....	0.833	0.865	12.6	4.2	16.8	1.510	0.49	0.992
Truck farm soil.....	0.910	0.902	13.9	5.0	18.9	1.481	0.61	1.044
Muck.....	0.811	0.853	11.0	3.9	14.9	1.330	0.49	0.877
Pure sand.....	0.815	0.949	7.9	4.2	12.1	0.980	0.44	0.687

* Treatment on Wooster silt loam has been as follows:

Lime has been applied in varying amounts since 1903.

Acid phosphate 320 pounds each 5-year period since 1894.

Muriate potash 260 pounds each 5-year period since 1894.

TABLE 4
Soil potassium soluble in 0.01 N HNO₃

SOIL AND TREATMENT	SOLUBLE POTASSIUM
	p. p. m.
Wooster silt loam; no treatment.....	34
Wooster silt loam; limed.....	23
Wooster silt loam; acid phosphate fertilizer.....	37
Wooster silt loam; acid phosphate fertilizer; limed.....	17
Wooster silt loam; muriate potash fertilizer.....	77
Forestry soil.....	88
Clyde clay.....	36
Truck farm soil.....	63

sandy soils are considered to be more responsive to potassium additions. These results with the two grains indicated that wheat was more satisfactory than rye.

Test of wheat grown in 100 gm. of soil

Table 3 gives results obtained by applying the Neubauer test to several soils. In this work 100 gm. of soil mixed with 50 gm. of sand was placed in the bottom of small pots and covered with 250 gm. of sand. Information regarding the dilute acid-soluble potassium content of some of the soils included in this test had previously been obtained from 0.01 normal acid extractions. The acid-soluble potassium figures are given in table 4. Wheat plants withdrew the largest amount from the Forestry soil, which contained the most soluble potassium. This soil is a part of the Wooster farm that has not been cropped, but that had been used as a forestry nursery for a few years and that has been treated with manure. The Clyde clay, with a high content of total potassium, contained no more dilute acid-soluble potassium than the unfertilized silt loam on which certain crops make a more decided response to potash fertilizer. Potassium removed by wheat plants from the Clyde clay soil, however, gave indications that this soil has an abundance of available potassium. This agrees with the crop response to potash in field practice. Removal of potassium by wheat plants from limed and unlimed portions of Wooster silt loam soil fertilized with acid phosphate does not give the same indication of less available potassium in limed soil that was obtained from dilute acid extraction of the soil. Potassium taken up by wheat seedlings from potash-fertilized plot reflects the larger amount of soluble residual potassium.

Varying proportions of soil and number of plants

Some wheat plants grown in pots of a larger diameter, 5 inches, and having a capacity for approximately 1000 gm. of sand made a more vigorous growth than plants in containers of sufficient size for 100 gm. of soil and 300 gm. of sand. The soil was not placed in the bottom of the pot as suggested by Neubauer, but was mixed with the total amount of sand. From this it was concluded that a larger volume, permitting more extensive root development, was an advantage, and a test was made to determine what soil dilution and number of plants would provide the most favorable condition for obtaining indications of available potassium. In this work 25, 50, and 100 wheat plants were grown in 1000 gm. of sand containing the amounts of soil stated in table 5. Potassium assimilated from the soil is represented by the amount in a given number of plants less that in the same number of plants grown in pure sand. These data for the actual amount of potassium assimilated from the soil are given in column 6 of table 5.

It will be noted that in no case is the excess of potassium directly proportional to the number of plants grown in a given soil dilution. Neither is there any correlation between potassium removed by a given number of plants and the degree of soil dilution. In fact the data indicate that 25 plants on 50 gm. of soil assimilate proportionately more of the soil potassium than do 50 plants

on 100 gm. of soil. For analytical purposes, 25 or 50 wheat plants do not produce sufficient material. The optimum number is 100. It was concluded

TABLE 5
Averaged results for wheat plants grown in varying proportions of soil mixed with 1000 gm. sand

SOIL	NUMBER OF PLANTS	DRY WEIGHT OF PLANTS	POTASSIUM IN PLANTS	POTASSIUM CONCENTRATION	POTASSIUM REMOVED IN EXCESS OF THAT IN SEEDS
gm.		gm.	mgm.	per cent	mgm.
50	25	0.823	5.8	0.699	2.1
50	50	1.547	10.0	0.649	2.0
50	100	2.801	13.8	0.492	0.2
100	25	0.881	5.6	0.632	1.9
100	50	1.579	8.9	0.566	0.9
100	100	2.754	14.9	0.541	1.3
200	25	0.937	6.7	0.714	3.0
200	50	1.698	9.2	0.598	1.2
200	100	3.205	17.6	0.548	4.0
Sand*	25	0.743	3.7	0.500	
Sand	50	1.409	8.0	0.568	
Sand	100	2.656	13.6	0.513	

* Results for sand representing available in seed.

TABLE 6
Potassium removed from fertility plot soils by wheat plants

SOIL TREATMENT IN FIELD*	DRY WEIGHT OF TOPS	POTASSIUM IN TOPS	POTASSIUM CONCENTRATION
	gm.	mgm.	per cent
None.....	1.149	8.5	0.738
Lime.....	1.351	12.1	0.896
Acid phosphate.....	1.593	14.5	0.908
Acid phosphate; lime.....	1.253	12.4	0.959
Muriate potash.....	1.388	17.2	1.142
Muriate potash; lime.....	1.354	18.9	1.397
Nitrate soda.....	1.111	11.9	1.068
Nitrate soda; lime.....	1.116	11.6	1.038
Manure.....	1.293	15.5	1.199
Manure; lime.....	1.367	16.2	1.189

* Lime as been applied in varying amounts since 1903. Fertilizer and manure additions for each 5-year period since 1894 have been as follows: Acid phosphate, 320 pounds; muriate potash, 260 pounds; nitrate soda, 440 pounds; manure, 16 tons.

from this test of soil dilutions that 200 gm. of soil in 1000 gm. of sand is better than a smaller amount, since this dilution produced the greatest amount of

plant material associated with the largest removal of potassium. It was found that the potassium content of 3.5 gm.—the average weight of 10 sets of 100 seeds—was 16.33 mg. This is in excess of the potassium taken up by plants grown in pure sand, and in plants grown in 50 or 100 gm. of soil.

Test of fertility plot soils

Some further tests with the seedling method were made of soils from several of the 5-year rotation fertility plots (4). Wheat plants were grown in 200 gm. of soil diluted with 1000 gm. of sand. On account of the difficulty of removing adhering soil from the roots, only the tops were weighed and analyzed.

The data for plants grown under these conditions are given in table 6. Inspection of the results shows that plants removed more potassium from soils of plots that contain potassium residual from muriate of potash and manure. Aside from these two soils there is no very significant relation between potassium removal and the fertilizer treatment.

Influence of additions

Usually when vegetation tests are made for the purpose of determining variations in supply of some essential element, it is considered necessary to insure the optimum condition for the other growth factors, by supplying an excess of the nutritive substances that are not under consideration. Although Neubauer states that this does not appear to affect the abstraction of nutritive substances by seedlings, some tests were made to determine what effect additions to soil would have on potassium removal from fertility plot soils that have been variously treated for a long continued period. In one series, available nitrogen was supplied by applying 0.143 gm. of sodium nitrate or an equivalent amount of ammonium sulfate to 200 gm. of soil mixed with 1000 gm. of sand. This amount is equivalent to 120 p.p.m. of sand and soil mixture. These nitrogen-carrying salts in solution were added to the soil 10 days previous to incorporating it with sand and planting the wheat. Water was added to bring the moisture content to 12 per cent, which was maintained throughout the experiment by daily additions through a small glass tube placed in the center of each pot.

The tabulated data for this series given in table 7 are the averaged results for triplicate pots of each treatment. As the weights of plant material produced, undoubtedly have an influence on the amount of potassium removed and its concentration in the plant, attention is directed to the influence of soil and of treatment on variations in weight of 100 plants grown on the several soils. Ammonium sulfate, on practically all of the soils, adversely affected growth of plants, as the weights of dry matter are less than for plants from pots receiving no additions of nitrate of soda or ammonium sulfate. This effect of ammonium sulfate was generally most pronounced on soils from unlimed portions of plots. Whether this effect was caused by increased

TABLE 7
Effect on wheat plants of additions of sodium nitrate and ammonium sulfate to fertility plot soils

SOIL TREATMENT IN FIELD*	POT ADDITION	DRY	POTAS-	POTAS-
		WEIGHT	S- IUM	S- IUM
		OF TOPS	IN TOPS	CONCEN- TRATION
		gm.	mgm.	per cent
No treatment.....	Sodium nitrate	1.280	12.7	1.007
	Ammonium sulfate	0.988	10.7	1.084
	No addition	1.149	8.5	0.738
Lime.....	Sodium nitrate	1.403	13.8	0.982
	Ammonium sulfate	1.235	13.5	1.088
	No addition	1.351	12.1	0.896
Acid phosphate.....	Sodium nitrate	1.532	15.6	1.016
	Ammonium sulfate	1.282	15.3	1.191
	No addition	1.593	14.5	0.908
Acid phosphate; lime.....	Sodium nitrate	1.381	13.9	0.989
	Ammonium sulfate	1.206	13.1	1.081
	No addition	1.253	12.4	0.959
Muriate potash.....	Sodium nitrate	1.726	20.3	1.179
	Ammonium sulfate	1.162	21.0	1.809
	No addition	1.388	17.3	1.142
Muriate potash; lime.....	Sodium nitrate	1.218	14.5	1.211
	Ammonium sulfate	1.159	14.5	1.254
	No addition	1.354	18.9	1.397
Nitrate soda.....	Sodium nitrate	1.163	12.8	1.104
	Ammonium sulfate	0.976	12.7	1.301
	No addition	1.111	11.9	1.068
Nitrate soda; lime.....	Sodium nitrate	1.312	11.0	0.840
	Ammonium sulfate	1.098	11.4	1.033
	No addition	1.116	11.6	1.038
Manure.....	Sodium nitrate	1.359	18.2	1.341
	Ammonium sulfate	1.049	16.6	1.584
	No addition	1.293	15.5	1.199
Manure; lime.....	Sodium nitrate	1.425	17.5	1.224
	Ammonium sulfate	1.385	17.4	1.262
	No addition	1.367	16.2	1.189

* Fertilizer and manure treatment of plots as stated in footnote table 6.

acidity or by physiological unbalance is not evident. Nitrate of soda produced more vigorous growth and a larger weight of plant material on all soils except those from the plot treated with acid phosphate and from the limed portion of the plot fertilized with muriate of potash. The comparative effect of sodium nitrate and ammonium sulfate on growth of wheat plants in this experiment is shown in plate 1.

It will be noted that although the yield of potassium in plant material was in some cases associated with a larger weight of plants, this was not uniformly so. Both sodium nitrate and ammonium sulfate additions to the limed and unlimed portions of unfertilized soil caused an increased potassium assimilation over that of plants from soil receiving no addition; this was true regardless of the dry weight, which was lowest with the ammonium sulfate treatment. In the case of unlimed soil from the acid phosphate fertilized plot, the pot with no addition gave the heaviest growth of plants, but the amount of potassium assimilated falls below that from the treated pots. Although ammonium sulfate has caused a decreased weight of plants on this soil, potassium removal was about the same as that of the plants grown in the pot that had an addition of sodium nitrate.

These additions also caused an increased potassium assimilation or removal from soils of the other plots, excepting from limed portions of plots fertilized with nitrate of soda and muriate of potash. The results for the latter plot show that the amount of potassium in plants from the pot that had no addition was noticeably more than in plants grown on this soil modified by additions of sodium nitrate and ammonium sulfate.

From the results for unlimed soil fertilized with potash it is quite apparent that this soil contains considerable residual potassium, and that both sodium nitrate and ammonium sulfate have increased the removal by wheat plants. Possibly base exchange may have been a factor influencing the larger removal of potassium from this soil. Ammonium sulfate retarded plant growth on this soil whereas nitrate of soda increased it, which accounts for the extreme variation in percentage or concentration of potassium in the plant material. When the growth medium was soil from the limed portion of the potash fertilized plot the results display an almost complete reversal of those obtained for the other soils of this series, for nitrate of soda and ammonium sulfate have not only retarded vegetative growth, but have also appreciably reduced the amount of potassium assimilated. An explanation of this may be that in the absence of other assimilable elements the plant draws more heavily upon an element available in larger quantity.

The potassium content of plants grown on manured soil furnishes indications of an available supply that is somewhat less than that in muriate of potash fertilized soil, but more than in the other soils.

Although the variations in potassium assimilation of wheat plants grown under modified conditions of treatment are not of sufficient magnitude to justify positive deductions, it would seem that the quantity of potassium in

wheat plants at the seedling stage is in a measure influenced by nutritional growth factors. If the results for plants from soils treated with ammonium sulfate are omitted, it is apparent that increased plant growth and content of potassium are closely in accord.

It is a question whether the total amount of potassium in plants or the concentration gives the more correct indications of available supply, or of the plant's capacity to assimilate potassium when growth factors are variable. Obviously the calculated concentration of potassium is dependent on the weight of plant material, so that although approximately equal amounts of potassium may be present in the same number of plants grown in the same quantity of soil, small differences in weights may affect the results calculated on a percentage basis. Neubauer apparently does not make deductions from concentration of potassium in plants.

A further test of the effect of available nutrients on plant growth and assimilation of potassium, included additions of mono-calcium phosphate and potassium chloride, as well as sodium nitrate and ammonium sulfate to several soils from fertility plots. In this series the proportions of soil and sand were the same as in the previous test, and the water content was maintained at 12 per cent. The amounts of salts added in solution to soils previous to diluting with sand and placing in pots were as follows: mono-calcium phosphate, 0.075 gm; potassium chloride, 0.15 gm; sodium nitrate, 0.143 gm; ammonium sulfate, 0.108 gm.

Mono-calcium phosphate furnished phosphorus equivalent to that in 250 pounds of acid phosphate per million of soil on the basis of sand and soil mixture. Potassium chloride at the rate of 0.15 gm. to a pot is equal to 125 pounds per million of soil. Sodium nitrate, 0.143 gm. per pot, is at the rate of approximately 120 pounds to one million of soil; 0.108 gm. of ammonium sulfate is equal to about 90 pounds per million of soil.

The wheat seedlings were grown for 20 days. The data for this series in table 8 exhibit decided variations in weights of dry plant material and potassium removal from the several soils included in this test. Ammonium sulfate and mono-calcium phosphate in contrast with sodium nitrate or potassium chloride additions on the same soil, adversely affected plant growth, so that less weight of plant material was produced. Sodium nitrate was most effective in promoting plant growth on soil from the plot previously fertilized with muriate of potash. This was also true for the previous series where sodium nitrate was added to soil from this plot.

Potassium chloride had a marked influence on stimulating the growth of wheat seedlings. Compared with the plants of the previous series grown in pots that had no addition, the weights of plants that received potassium chloride were consistently increased. The remarkable stimulation of growth on unfertilized soil by potassium chloride in contrast with phosphate, ammonium sulfate, and sodium nitrate additions is illustrated in plate 2. The growth made by plants on unfertilized soil and on soil from plots that have

TABLE 8

Effect on wheat plants of addition of mono-calcium phosphate, potassium chloride, sodium nitrate, and ammonium sulfate to soils

SOIL AND TREATMENT IN FIELD*	FOT ADDITIONS	DRY WEIGHT OF TOPS	POTAS- SIUM IN TOPS	POTAS- SIUM CONCEN- TRATION
		gm.	mgm.	per cent
5-year rotation. No treatment	Sodium nitrate	1.218	7.5	0.614
	Ammonium sulfate	1.034	8.4	0.805
	Mono-calcium phosphate	1.234	11.1	0.910
	Potassium chloride	1.825	65.2	3.583
5-year rotation. Lime	Sodium nitrate	1.447	11.2	0.817
	Ammonium sulfate	1.175	11.2	0.979
	Mono-calcium phosphate	1.233	12.9	1.051
	Potassium chloride	1.773	65.0	3.666
5-year rotation. Acid phosphate	Sodium nitrate	1.549	14.7	0.951
	Ammonium sulfate	1.534	8.9	0.582
	Potassium chloride	2.038	73.3	3.596
5-year rotation. Acid phosphate; lime	Sodium nitrate	1.419	12.9	0.907
	Ammonium sulfate	1.371	7.9	0.575
	Potassium chloride	1.469	43.5	2.968
5-year rotation. Muriate potash	Sodium nitrate	1.891	22.6	1.195
	Ammonium sulfate	1.493	16.9	1.136
	Mono-calcium phosphate	1.341	21.2	1.581
5-year rotation. Muriate potash; lime	Sodium nitrate	1.575	19.3	1.226
	Ammonium sulfate	1.355	13.8	1.021
	Mono-calcium phosphate	1.212	19.1	1.581
5-year rotation. Nitrate soda	Sodium nitrate	1.534	14.2	0.928
	Ammonium sulfate	1.224	13.4	1.097
	Mono-calcium phosphate	1.250	16.4	1.315
	Potassium chloride	1.491	60.5	4.061
5-year rotation. Nitrate soda; lime	Sodium nitrate	1.601	14.6	0.914
	Ammonium sulfate	1.268	11.8	0.932
	Mono-calcium phosphate	1.348	14.3	1.057
	Potassium chloride	1.581	63.4	4.408
5-year rotation. Acid phosphate; nitrate soda	Mono-calcium phosphate	1.228	12.4	1.053
	Potassium chloride	1.525	35.1	2.301
5-year rotation. Acid phosphate; nitrate soda; lime	Mono-calcium phosphate	1.262	14.6	1.161
	Potassium chloride	1.757	70.0	4.009

* Fertilizer treatment of plots for each 5-year period since 1894 as follows: Acid phosphate 320 pounds per acre; muriate of potash 260 pounds; nitrate of soda 440 pounds; manure 16 tons. Treatment for each 3-year rotation period since 1896; Acid phosphate 320 pounds per acre; nitrate of soda 200 pounds.

TABLE 8—*Continued*

SOIL AND TREATMENT IN FIELD*	POT ADDITIONS	DRY WEIGHT OF TOPS	POTASSIUM IN TOPS	POTASSIUM CONCENTRATION
		gm.	mgm.	per cent
5-year rotation. Manure	Mono-calcium phosphate	1.232	17.7	1.433
5-year rotation. Manure; lime	Mono-calcium phosphate	1.281	17.0	1.326
3-year rotation. No treatment	Potassium chloride	1.805	84.7	4.688
3-year rotation. Acid phosphate	Potassium chloride	1.569	74.7	4.763
3-year rotation. Acid phosphate; nitrate soda	Potassium chloride	1.558	81.9	5.274
Forestry plot soil	Potassium chloride	2.113	82.0	3.919

been fertilized singly with nitrate of soda, acid phosphate, and muriate of potash can be seen from the photographs of wheat plants (plate 3). On the muriate of potash fertilized soil that had no additions at the time of growing the wheat seedlings, the residual potassium evidently stimulated the growth of the young wheat plants. Although addition of sodium nitrate caused a greater weight of plants on several of the soils, the removal of potassium was not increased except from the soils of plots previously fertilized with muriate of potash and nitrate of soda.

Mono-calcium phosphate apparently increased the amount of potassium in wheat seedlings. Regardless of the effect of this addition on the growth and weight of plants, larger amounts of potassium, and increased concentration over untreated soil resulted where mono-calcium phosphate was added.

Potassium chloride had the most marked influence on potassium content, and also appreciably increased the weights of plants grown on several soils. Although the amount added was comparatively small—0.078 gm.—the young plants assimilated potassium in excess of their requirements. From certain of the soils, the plants contained potassium in excess of the soluble potassium added, which would seem to indicate 100 per cent recovery.

The data for plants grown on soil that had previously been fertilized with muriate of potash indicate a luxury consumption of potassium, since an increased potassium content is not always associated with greater weight of plants.

The results for some of the treatments show that there is an inverse relation between plant weight and potassium content. If the growth of plants is influenced by the supply or deficiency of one or more essential elements, the amount of potassium in plants may vary, although the amount is the same in different soils or in the same soil modified by treatment.

Potassium assimilated by wheat and buckwheat

In this test 10 plants to a pot were grown in different soil dilutions for 20 days. Plants were grown in 50, 100, and 200 gm. of soil mixed with sufficient sand to give a total weight of 1600 gm. in each pot. Plants were also grown in pure quartz sand and in soil with no dilution. The results obtained from wheat and buckwheat are given in table 9.

It will be noted that in 200 gm. of soil the increased weight of buckwheat plants was more marked, but with smaller amounts of soil the differences between weight of wheat and of buckwheat decreased.

With less than 200 gm. of soil the potassium content of 10 wheat plants was the same, but there were gradually increasing amounts of potassium in the buckwheat, resulting in a rather consistent relation between the production of plant material and the potassium assimilated. It is evident from the amounts of potassium removed by wheat and buckwheat grown for the same length of time, that buckwheat draws more heavily on soil potassium. The

TABLE 9
Data for wheat and buckwheat plants grown in varying proportions of soil and sand

WEIGHT OF SOIL	DRY PLANT WEIGHT		POTASSIUM IN TOPS		POTASSIUM CONCENTRATION	
	Wheat	Buckwheat	Wheat	Buckwheat	Wheat	Buckwheat
gm.	gm.	gm.	mgm.	mgm.	per cent	per cent
0	0.303	0.307	3.8	3.7	1.246	1.200
50	0.358	0.551	3.7	5.1	1.032	0.918
100	0.433	0.761	3.9	7.3	0.909	0.961
200	0.669	1.251	5.7	14.2	0.860	1.131
1,600	1.977	3.579	22.8	49.5	1.151	1.384

more marked increased growth of buckwheat as compared with wheat in the several soil dilutions is shown in plate 4. Some preliminary experiments reported by Haley (1) have indicated that buckwheat is satisfactory for measuring the availability of potassium in soils.

Potassium removal by corn plants

In some further work, corn plants were grown in soil from fertility experiment plots. In one test 5 corn plants were grown for 18 days in 800 gm. of soil diluted with 4000 gm. of sand. The soils were from unlimed and limed portions of an unfertilized plot, and from plots that had been fertilized with muriate of potash and with acid phosphate. From the results in table 10 it is apparent that sodium nitrate and ammonium sulfate added to supply available nitrogen and bases for replacement reactions apparently have had little or no effect.

The more marked variations in potassium removed were found in the corn plants grown on soil from plots fertilized with acid phosphate and with muriate

TABLE 10
Potassium removal by 5 Corn Plants grown for 18 days in 800 gm. soil mixed with 4000 gm. sand

SOIL TREATMENT ON PLOTS*	POT ADDITIONS	WEIGHT		POTASSIUM REMOVED	
		Tops	Roots	Tops	Roots
		gm.	gm.	mgm.	mgm.
None.....	None	1.11	2.05	13	12
	Sodium nitrate	1.18	2.12	12	11
	Ammonium sulfate	1.05	2.13	9	7
Lime.....	None	1.16	2.48	17	17
	Sodium nitrate	1.11	2.17	13	14
	Ammonium sulfate	1.31	2.57	23	16
Acid phosphate.....	None	0.92	1.60	8	8
	Sodium nitrate	0.87	1.84	9	6
	Ammonium sulfate	0.81	1.64	8	7
Acid phosphate; lime.....	None	1.06	1.84	8	9
	Sodium nitrate	0.82	1.79	7	8
	Ammonium sulfate	0.84	1.83	8	7
Muriate potash.....	None	0.93	1.72	21	15
	Sodium nitrate	1.02	1.67	22	17
	Ammonium sulfate	1.07	1.84	26	22
Muriate potash; lime.....	None	0.91	1.79	15	14
	Sodium nitrate	0.73	1.73	11	10
	Ammonium sulfate	0.72	1.56	10	9
Sand.....	None	0.29	1.27	4	5

* Treatment of plots same as stated in footnote table 6.

TABLE 11
Potassium removed by corn and wheat plants grown for 18 days

SOIL TREATMENT IN FIELD	POTASSIUM REMOVED BY		CENTI-NORMAL ACID-SOLUBLE POTASSIUM <i>p.p.m. soil</i>
	Wheat	Corn	
	mgm.	mgm.	
None.....	8	13	34
Lime.....	12	17	23
Acid phosphate.....	14	8	37
Acid phosphate; lime.....	12	8	17
Muriate potash.....	17	21	77
Muriate potash; lime.....	19	15	36

of potash. In table 11, the results for 5 corn plants grown in 800 gm. of soil diluted with 4000 gm. of sand are compared with the removal by 100 wheat plants grown in 200 gm. of soil and 1000 gm. of sand. Although the ratio of soil to sand was the same for corn and wheat the former had more soil,

TABLE 12
*Potassium removed by 2 corn plants grown in undiluted soil from fertility experiment plots—
Planted June 3, cut July 25*

SOIL AND FERTILIZER TREATMENT*	POT ADDITIONS	WEIGHT OF TOPS	POTAS- SIUM REMOVED	POTAS- SIUM CONCEN- TRATION
		gm.	mgm.	per cent
5-year rotation:				
None.....	None	15	154	1.025
None.....	Acid phosphate; sodium nitrate	25	188	0.752
None.....	Acid phosphate; sodium nitrate; potassium chloride	30	512	1.705
Acid phosphate.....	None	18	146	0.812
Acid phosphate.....	Potassium chloride	25	346	1.383
Acid phosphate.....	Sodium nitrate; potassium chloride	17	281	1.653
Muriate potash.....	None	15	311	2.075
Muriate potash.....	Acid phosphate	20	343	1.717
Muriate potash.....	Acid phosphate; sodium nitrate	20	332	1.661
Acid phosphate; sodium nitrate...	None	15	148	0.989
Acid phosphate; sodium nitrate...	Potassium chloride	19	289	1.520
3-year potato rotation:				
None.....	None	19	177	0.929
None.....	Potassium chloride	22	319	1.452
Acid phosphate.....	None	15	116	0.772
Acid phosphate.....	Potassium chloride	20	286	1.431
Acid phosphate.....	Potassium chloride; sodium nitrate	30	362	1.206
Muriate potash.....	None	15	259	1.725
Muriate potash.....	Acid phosphate; sodium nitrate	25	277	1.109
Forestry plot	None	32	678	2.119
Forestry plot.....	Acid phosphate	39	756	1.938

* Fertilizer treatment of plots for each 5-year period since 1894 as follows: Acid phosphate 320 pounds per acre; muriate potash 260 pounds; nitrate soda 440 pounds. Treatment for each 3-year rotation period since 1896: Acid phosphate 320 pounds; muriate potash 200 pounds.

and consequently more potassium at its disposal. If the dilute-acid-soluble potassium furnishes reliable evidence of variations in availability, the corn plant in this test has been no more satisfactory than wheat in furnishing indications of the characteristics of the soil in this respect.

Potassium removal by corn plants grown in undiluted soil

Corn plants were grown in undiluted soil from the several fertility experiment plots indicated in table 12. The soil used in this test was from the portions of the plots that have received additions of limestone. Triplicate pots containing 3000 gm. of soil were planted June 3 and harvested July 25. Five plants were started in each pot and at the end of the first week the plants were thinned to two.

Additions of acid phosphate, potassium chloride, and sodium nitrate were made to certain pots as indicated in the table 12. The quantities of these materials per pot were as follows: Acid phosphate 0.9 gm.; potassium chloride 0.375 gm.; sodium nitrate 0.357 gm. These quantities are equivalent to 300 p.p.m. of acid phosphate, 125 p.p.m. of potassium chloride, and 119 p.p.m. of sodium nitrate. Sodium nitrate and potassium chloride were added in solution, and acid phosphate was mixed with the soil 10 days before planting the corn. Triplicate tests of each soil were made and the results averaged for the three pots.

The object of this test was to determine to what extent corn plants grown for a more extended period than the plants in previous tests would reflect variations in potassium supply brought about by fertilizer treatment, especially by that not including potassium. The additions to the pots provided for a supply of available nutrients other than those with which the plots had been fertilized.

The weights of plants on the several soils are not widely different with the exception of those on the forestry plot soil, which exhibited a high productive power whenever it has been used in the pot tests with wheat seedlings. With additions of phosphorus, potassium, and nitrogen to the soils in the pots just previous to planting the corn, there were, however, some increases in weights of plants produced. The addition of potassium chloride to the soil from a plot fertilized with acid phosphate caused an increase, whereas the addition of sodium nitrate with potassium apparently adversely affected the growth, resulting in a plant weight equal to that on the soil with no addition. The potassium removed, however, was more than that of plants grown in the same soil without additions.

Regardless of the effect on weight of dry matter produced, potassium chloride invariably caused an increased removal of potassium, as well as a greater concentration than in plants grown on soil receiving no addition of available potassium. The increased amount of potassium taken up by plants grown on soil that had been fertilized with muriate of potash also reflects the larger available supply, although the yield of dry plant material did not differ materially from that of plants on unfertilized soil.

In this comparison of soils from the several fertility plots no check with sand only was included. But a check on that portion of the potassium removed that could have been obtained from the seed is furnished by available

data regarding the weight and potassium content of an average sample of seed planted in this and in the previous test with corn. The average weight of the corn was 0.2552 gm. per kernel, and the potassium content per gram of seed was 0.003 gm., so that 2 seeds supplied 1.5 mgm., a negligible quantity in comparison to the total amount removed. These corn plants grown in undiluted soil have assimilated varying amounts of potassium, which quite consistently indicate differences in the available supply.

SUMMARY

Experiments have been in progress to ascertain whether potassium abstracted by plants will furnish reliable information concerning the available supply in soils.

Neubauer's seedling method of soil analysis, in which a large number of plants are grown in a small amount of soil diluted with sand, has been employed.

The soils used in measuring the availability of potassium by means of plant seedlings included those from fertility experiment plots that have been fertilized and under observation for a period of years.

Several series of tests were made varying somewhat as to the soil dilution with sand, the number of plants, and other conditions.

From a comparison of rye and wheat, it was found that the latter produced a larger weight of plant material and removed more potassium.

It was concluded from experiments with varying proportions of soil and sand, and with varying numbers of plants, that 100 wheat seedlings grown in 200 gm. of soil diluted with 1000 gm. of sand furnished the optimum conditions.

A test with wheat and buckwheat plants grown for 20 days showed that buckwheat abstracted more potassium.

Additions of available nutrients to soils that have been fertilized and cropped for many years affected the potassium removal.

It is apparent that the amount of potassium removed is closely associated with increased plant growth produced by supplying available nutrients.

Additions of available potassium had a marked influence in stimulating the growth of wheat seedlings.

From the increased potassium removed by wheat seedlings grown on soil that have received applications of potassium in fertilizers and manure, it is evident that a potassium residual from that applied is readily available.

Potassium abstracted by wheat seedlings from limed soil that has received no other fertilizer than acid phosphate for over 30 years, does not indicate the same depletion of available potassium as do a dilute acid extraction of the soil and decreased corn yields during recent years.

The potassium content of corn plants grown beyond the seedling stage in undiluted soil varied very consistently with the available supply, as indicated by the fertilizer treatment and the additions to pots.

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PLATE 1

EFFECT OF AMMONIUM SULFATE AND SODIUM NITRATE ADDITIONS ON GROWTH OF WHEAT SEEDLINGS

Pot 28, ammonium sulfate; pot 27, sodium nitrate



PLATE 2

EFFECT OF LIMING ON THE GROWTH OF WHEAT SEEDLINGS

FIG. 1. Unlimed soil. Pot 2, mono-calcium phosphate; pot 21, potassium chloride; pot 53, ammonium sulfate; pot 45, sodium nitrate.

FIG. 2 Limed soil. Pot 3, mono-calcium phosphate; pot 23, potassium chloride; pot 54, ammonium sulfate; pot 46, sodium nitrate.



FIG. 1



FIG. 2

PLATE 3

GROWTH OF WHEAT SEEDLINGS ON SOILS FROM 5-YEAR ROTATION PLOTS

FIG. 1. Pot 61, unfertilized soil; pot 65, plot 2, acid phosphate.

FIG. 2. Pot 69, plot 3, muriate potash; pot 73, plot 5, sodium nitrate.



FIG. 1



FIG. 2

PLATE 4

GROWTH OF BUCKWHEAT AND WHEAT IN SEVERAL SOIL DILUTIONS

FIG. 1. Buckwheat. Pot 1, sand; pot 2, 50 gm. soil; pot 3, 100 gm. soil; pot 4, 200 gm. soil; pot 5, soil, no dilution.

FIG. 2. Wheat. Pot 11 sand; pot 12, 50 gm. soil; pot 13, 100 gm. soil; pot 14, 200 gm. soil; pot 15, soil, no dilution.

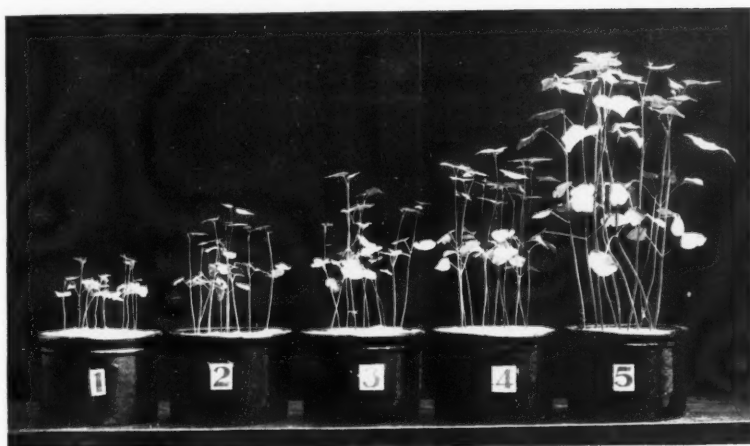


FIG. 1

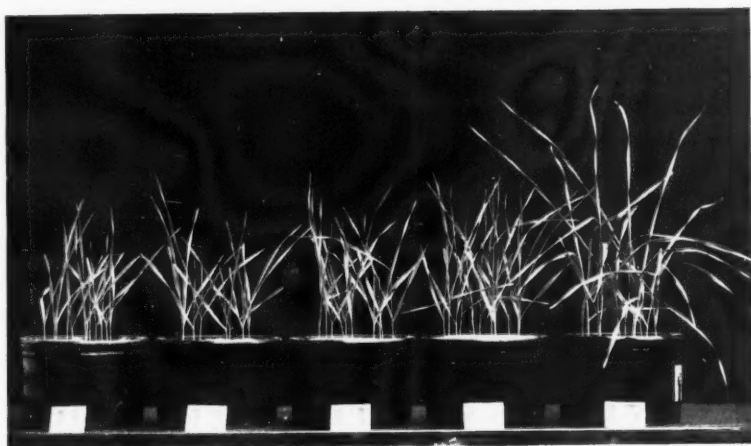


FIG. 2



EFFECTS OF SOME ELECTROLYTES ON KAOLIN AND THE PROBABLE RELATION TO THE SOIL

JOHN R. SKEEN

*University of Pennsylvania*¹

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In a previous paper (22) evidence was presented indicating that the formation of hardpan in clay soils was a function of the pH. In soils observed in the vicinity of Philadelphia, the clay particles forming the hardpan are bound either by iron or aluminum, as the oxides or silicates. They present a layer that is practically impermeable to water and are a factor in local plant distribution, because, severed from the connection with the subsoil, they can dry out more thoroughly and thus cause a higher osmotic pressure, and, it was believed, because iron and aluminum were in the soil solution in sufficient quantities to be toxic to some plants. In a recent article Magistad (15) contributed toward the toxicity problem. This paper deals with a preliminary physical chemical consideration of the behavior of kaolin in an effort to explain how hardpans are formed in acid clay soils.

NATURE OF THE HARDPAN

The hardpan in question occurs in silt and clay loams which have become acid. It is found as a red or silvery layer at various distances below the surface, but is most common at depths of 6 to 20 inches. The layer is made up of clay aggregates more or less cemented by the silicates and oxides of aluminum and iron. When dry, the layer is exceedingly hard, and, soaked in water, becomes tough. In both conditions it is impermeable to water so that the surface soil, even a short time after a rain, loses most of its capillary moisture, while the subsoil immediately below the layer generally has a maximum supply.

In the Philadelphia region, where this hardpan occurs, no succulents survive the summer months.

The surface 6 inches of the soil is generally coarsely granular and dry and relatively free of organic matter. When saturated it tends to puddle and is most unsatisfactory to work.

ADAPTABILITY OF KAOLIN FOR EXPERIMENTS

Several methods of fractionating soils were tried but the same type and size of particle was not consistently obtained. Although, in all the soils used,

¹Department of Botany.

when well washed in distilled water, the particles migrated toward the anode in an electric field, yet they migrated at different rates in samples of soil prepared in the same way at different times. Results obtained with one sample could not be compared with observations made on a different batch of what was apparently the same material. As reproducible results are imperative, it is necessary that the material be of a uniform quality. Soil samples proved impractical and as a substitute, the kaolin supplied by Merck and Company was used. It is fairly uniform in texture and chemically is nearly free of everything except HCl.

It is believed that any conclusions that may be drawn when kaolin¹ is used as the medium are applicable to "clays" as a class. According to Washburn (27), one of the most common mineralogical constituents of "clay" is kaolin, which in its purest form is a crystalline mineral having the composition $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$. Warington (26) states that "in a typical clay (kaolin) derived from the decomposition of feldspar, the whole substance has practically the same chemical composition. . . ." Merrill (18) says, "orthoclase is one of the commonest and most abundant of the feldspars and forms an essential constituent of acid rocks. . . . As a rock constituent, the potash feldspars are of primary importance yielding on their decomposition . . . the material kaolin. . . ."

According to Hall (6) and Hilgard (9) orthoclase may be written $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$. It decomposes in carbonated water forming kaolinite, $\text{Al}_2\text{O}_2(\text{OH})_4 \cdot \text{Si}_2\text{O}_3$, the basis of clay. Swanson (23) gives another formula for kaolinite and graphically writes it differently from other authorities. It has been suggested that kaolin may be a loose Van Bemmelen (24, 25) adsorption compound of aluminum oxide and sand which may behave as a unit although it is not necessarily one.

The structure of kaolin seems doubtful but it is an important constituent of nearly all clay soils.

METHODS

Determinations were made simultaneously on the same sample of kaolin for:

1. Turbidities at intervals up to forty minutes,
2. Final volumes of the sedimented kaolin at various intervals up to two days,
3. Conductivity, always comparing to blanks containing no kaolin,
4. pH,
5. Sign and intensity of the charge on the particles.

The kaolin was put into collodion bags and dialyzed in a stream of running water for eight weeks. The conductance of the supernatant liquid in which the kaolin was kept was only slightly lower than that of distilled water exposed the same length of time although protected from dust. It was believed that the kaolin so prepared was "chemically pure" and that it did not ionize appre-

ciably. Kaolin was later prepared in an electric dialyzer (17), and washed several times by decantation. So prepared, its resistance is practically the same as that of freshly distilled water. A stock was thus easily prepared.

Determined stock solutions of aluminium chloride, calcium chloride, barium chloride, sodium chloride, hydrochloric acid, and sodium hydroxide were made up and the same solutions were used throughout the work. The sodium hydroxide solution was redetermined from time to time. The stock solutions were diluted with distilled water to give the required concentrations. The concentrations of the other solutions used were only approximately accurate.

A large number of 50-cc. graduated cylinders were procured and twenty chosen having the same internal depth, so that the internal friction in any check experiments would be the same through any given time interval. By means of a pipette, 2 gm. of kaolin were put into each of these graduates, and made up to the 50-cc. mark with the proper solution. In all cases two graduates with kaolin and distilled water were prepared as a check. The graduates were then tightly stoppered by inverting slightly oversize, pliable rubber stoppers into the openings. In this way the stoppers made a flat surface entirely across the mouth of the cylinders. This prevented kaolin from sticking to the much greater surface exposed by variously tapering stoppers. It was assumed that the same quantity of kaolin adhered to the stoppers in all cases. An error was introduced, but a constant one well within the limit of accuracy demanded by the experiments.

1. Turbidities as determined in these experiments are entirely comparative. The standard of comparison chosen was distilled water. Six concentrations of three electrolytes were generally prepared simultaneously when strictly comparative data was wanted. The kaolin was thoroughly shaken in the graduates three or four times at intervals before observations were made. Turbidities were compared at 2, 4, 7, 10, 15, 20, 25, 30, and 40 minutes and, when necessary, longer. The graduates were placed in front of a bank of 25-watt lamps. Black paper was placed behind the graduates so that a good contrast could be had under uniform conditions. After some little practice, it was possible to determine by simply observing turbidities, not only the concentration of the solutions but which solutions were in any given cylinder.

2. The volumes occupied by the kaolin in falling were determined at the same intervals as the turbidities and also at 12, 24, and 48 hours. The bulk of the kaolin settled together leaving a more or less dense supernatant liquid.

3. When the liquid was entirely clear, it was pipetted out and put into a tall, narrow beaker having a capacity of about 30 cc. The resistance in ohms of the liquid was recorded. The resistance in ohms of the same concentration of the liquid before determined, treated in the same way but with no addition of kaolin, was obtained. This gave an immediate and exact comparison of the degree of adsorption or non-adsorption of the electrolyte by kaolin.

4. Determinations for pH were made by means of the potentiometer using

a saturated calomel cell. With the unbuffered solutions, results were entirely unreliable and only those results are recorded which are dependable.

5. Migration measurements were made by means of the apparatus recommended by Northrop (21). The cell used had a depth of 0.2 mm. The particles were observable under the low power of the microscope and migrated at a fair rate in an electric field of 110 volts and 0.3 amperes. The field of the scope was graduated and a graduated glass disc was inserted just beneath the eye piece. By means of a stop watch it was then possible to determine the time required for particles to move a given distance. No observations were made on particles within 55μ of the upper and lower surfaces of the cell. Thus starting at a depth of 55μ from the top of the cell, determinations were made at intervals of 10μ at 10 depths. As many determinations of the rate of movement of the particles as possible were made at all the depths mentioned with the same sample. Because of the rapid settling of the particles, very few determinations could be made in some solutions at the upper levels. In such cases samples were made until the speed of at least ten particles could be observed.

The poles were changed at intervals and the rate of migration noted in the opposite direction. The mean rate of all depths of three or more separate experiments are recorded for each concentration used. As the particles are far from spherical and as in some solutions they form aggregates whereas in others they are very much dispersed, no attempt to calculate the intensity of the charge was made. In all cases the rates recorded are relative to the rate of migration of particles in distilled water.

The figures recorded in table 1 are believed dependable for the weaker solution, but are not satisfactorily reproduced at concentrations of 0.1 *M* or more. Particularly is this true in the case of HCl.

RESULTS

The results reported in table 1 are believed typical for kaolin treated as described. The figures for resistance are the mean of many determinations made on at least three separate check experiments. Final volume results are the mean of two or more readings on at least five check experiments. This also applies to the data on turbidity. It was hoped that pH determinations would be sufficiently accurate to indicate the possibility of the selective adsorption of ions by kaolin. As no reasonable checks were obtained, only the pH limits of the solutions of salts are recorded.

1. It was found that the effects of different solutions on the quantity of kaolin suspended were most apparent 15 minutes after the last shaking. As the bulk of the kaolin settled in the graduates there remained suspended sufficient kaolin particles to color the liquid. A liquid such as 0.001 *M* Al cleared immediately after shaking. The "turbidity" of this solution is recorded as 0. Less clear solutions were arbitrarily assigned a number as they

TABLE 1

MOLAR SALT CONCENTRATION	OHMS - KAOLIN	OHMS + KAOLIN	VOLUME OF SEDI- MENT AT 24 HOURS	TURBIDITY AT 15 MINUTES	TURBIDITY AT 30 MINUTES	SPEED PER SECOND	pH
Water	80,000	13,500	cc. 7.30	7	2	μ -14.5	8.4
NaOH	1.0	6	5.94	5	1	-12.9	
	0.3	13	5.58	6	1	-14.5	
	0.1	41	5.67	7	2	-16.7	
	0.03	114	6.75	7	3	-20.5	
	0.01	396	6.93	14	6	-26.0	
	0.003	1,755	6.39	28	12	-28.0	
NaCl	1.0	12	6.25	10	2	-10.4	8.4
	0.3	25	5.72	9	3	-23.3	
	0.1	76	6.24	9	3	-24.5	
	0.03	232	7.34	8	2	-21.6	
	0.01	716	7.44	7	2	-21.6	
	0.003	1,912	7.45	6	2	-20.2	8.5
HCl	1.0	3	5.58	7	1	+16.0	
	0.3	7	6.00	6	1	+	
	0.1	22	6.84	2	1	-	
	0.03	61	7.59	2	1	-	
	0.01	205	7.23	3	1	-	
	0.003	600	6.78	4	1	-11.3	
CaCl ₂	0.6	12	5.86	9	1	+8.9	7.5
	0.1	45	6.30	4	1	-5.7	
	0.03	132	6.43	3	1	-7.1	
	0.01	450	6.68	3	1	-8.6	
	0.003	1,080	6.68	4	1	-10.2	
	0.001	3,040	6.76	5	1	-10.3	
BaCl ₂	0.6	10	5.76	9	2	+3.0?	
	0.1	44	6.35	6	1	-4.5	
	0.03	120	6.61	4	1	-	
	0.01	376	6.61	2	1	-7.7	
	0.003	1,020	6.53	3	1	-10.8	
	0.001	3,340	6.53	4	1	-12.9	
AlCl ₃	0.6	7	6.52	11	4	+6.9	2.07
	0.1	21	7.94	8	3	+19.2	
	0.03	62	8.86	8	3	+29.5	
	0.01	190	8.90	8	3	+29.5	
	0.003	433	9.92	7	2	+32.0	
	0.001	1,210	10.74	0	0	+21.2	
	0.0003	3,040	8.02	2	1	-12.3	8.00

increased in turbidity. At 15 minutes from shaking, the graduate containing 0.3 *M* NaOH was less turbid than the graduate containing water. The value 6 is assigned for the turbidity of 0.3 *M* NaOH and 7 for kaolin and distilled water. The turbidity value for water is kept constant for the comparison of check experiments.

The turbidity value of kaolin in water after the 30-minute interval is placed at 2, and perfect clarity of the supernatant liquid at 0.

It is then clear that in all the solutions recorded in table 1 (except NaOH) the particles of kaolin settle more or less rapidly. It is also evident that different concentrations of the same electrolyte affect turbidities to a marked extent. With HCl, CaCl₂, BaCl₂, and AlCl₃ there is a concentration producing the least turbidity. Any increase or decrease from this concentration results in an increase in turbidity. It is significant to note that the least concentrated solution of NaCl produces the clearest solution, whereas the most concentrated solution of NaOH produces the least turbidity.

Al is the most efficient ion in clearing solutions of kaolin, followed by Ba, Ca, and H in the order given. With turbidities as criteria, the efficiency of the ions in clearing solutions reduced to simplest terms if H-1, Ba-3, Al-100. Ca is less efficient than Ba in this regard.

NaCl and particularly NaOH, greatly increase the turbidities of the solutions. Even traces of NaOH have a marked effect on kaolin, keeping quantities in suspension for two hours or longer.

Sodium sulfate behaves as NaOH, greatly increasing the turbidity of the solutions. Sodium citrate, even in concentrations of 0.001 *M*, causes the greatest increase in turbidity and prevents clearing for 10 days and sometimes longer.

Sucrose and urea have no effect on turbidities in weaker concentrations. The increase in the specific gravity of the more concentrated solutions tends to keep the particles in suspension for a slightly longer time than distilled water. Thus non-electrolytes have no effect on the clarity of the supernatant liquid.

These results are entirely as could be predicted and are used only as checks on the effect of ions of different speed and valency and as criteria of the relative degree of disassociation of the kaolin aggregates.

2. The concentrations of less than 0.03 *M* Na and H have approximately the same aggregate result, that is, little changing of the final volume of the sediment as compared to water. The OH ion decidedly decreases the final volume of the sediment as do the Ca and Ba ions. The SO₄ ion has a marked reducing effect on the final volume of the sediment whereas the tri-valent citrate ion reduces the volume by almost 50 per cent.

Of the ions used, Al alone increases the volume of the sediment to a marked extent.

The more concentrated solutions of all the salts used decrease the final

volume of the sedimented kaolin very considerably either compared to water or to the less concentrated solutions of the same salt.

Sucrose and urea had no effect whatever on the volume of the sediment produced, the values obtained in all concentrations being the same as those obtained with water. Having no tangential value, the curves are not drawn.

From the curves of figure 1, it may be seen that the volume occupied by 2 gm. of kaolin may be only 60 per cent of that volume attained in water, or it may have increased 50 per cent. Microscopic examination shows that such great differences are due to the formation of sizable aggregates in the case of the greatest increase in the final volume of the sediment, and to the complete break-up of the aggregates when the final volume is markedly decreased.

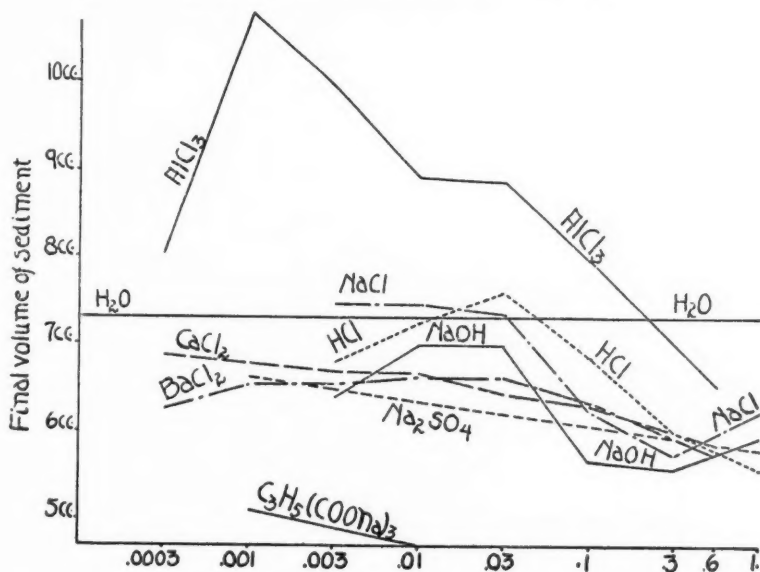


FIG. 1. FINAL VOLUME OF SEDIMENTED KAOLIN IN GRADUATES AT END OF 24 HOURS AFTER SHAKING WITH MOLAR CONCENTRATIONS OF ELECTROLYTES INDICATED

In a general way, it may be said that the more turbid is the supernatant liquid, the less will be the final volume of the sediment.

The experiments on turbidities and sediment volumes furnish a fair check on each other, and are important to this paper only as they indicate that the degree of aggregation of the kaolin particles can be markedly altered, that active anions can break up the aggregates—a tri-valent anion most completely, and a di-valent anion to a greater extent than the OH ion. Of the cations used, Al and Na alone cause the flocculation of the particles.

3. Figures 2 and 3 show that in the weaker solutions of the electrolytes (HCl excepted) no adsorption of the electrolytes occurs. On the contrary,

the solutions apparently become more concentrated in the presence of kaolin. These findings are in accord with those of many investigators working with substances other than kaolin, and again demonstrate that the Freundlich adsorption isotherm does not hold for dilute solutions.

No comparison of adsorption rates of the electrolytes can be made by this method, insofar as adsorption occurs only in the more concentrated solutions where the conduction is too great for accuracy. However, the method furnishes a good comparison of the "negative adsorption" of the salts. This seems to be a false term, for in such solutions something must be adsorbed—if not the solute, then the solvent. However, the following "negative adsorption" sequence may be written: $\text{NaCl}, \text{NaOH} > \text{BaCl}_2 > \text{AlCl}_3, \text{HCl}$, in which HCl is adsorbed at all concentrations.

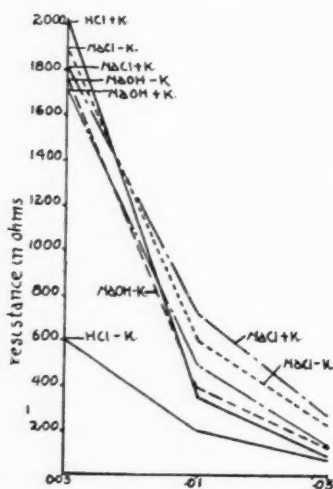


FIG. 2. RESISTANCE IN OHMS OF SOLUTIONS WITH AND WITHOUT KAOLIN AT VARIOUS MOLAR CONCENTRATIONS

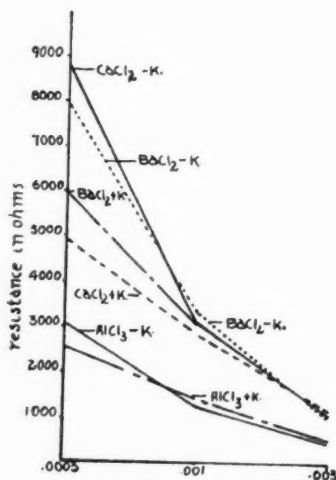


FIG. 3. RESISTANCE IN OHMS OF SOLUTIONS WITH AND WITHOUT KAOLIN AT VARIOUS MOLAR CONCENTRATIONS

It is significant to note that adsorption occurs in weaker solution of Al than of Ba and Ca. A fairly concentrated solution of Na must be present before it is adsorbed by kaolin.

4. The pH of kaolin when dialyzed as described is slightly greater than 8.4. Dilute solutions of the chlorides of Na, Ba, and Ca have little effect on this value. Increased concentrations of AlCl_3 rapidly decrease the pH of the kaolin solution but as the curve obtained is very irregular and is believed to be unreliable, it is not recorded. The few pH values reported were checked innumerable times and consistently gave the same figures. They are believed to be reliable, and are accurate within quite narrow limits. Ba behaves practically as Ca.

5. Cataphoretic measurements are reported in microns per second. The accuracy of the values given depends entirely on the number of determinations made at the different levels. The greater the number of determinations, the less is the chance of error and the closer is the approach to an absolute comparison. Most of the figures given represent an average of more than 100 observations at 10 levels from three or more separate samples. Comparative results are reproducible within narrow limits, but there is difficulty in obtaining specific values.

A considerable error is obtained in the more concentrated solutions, because

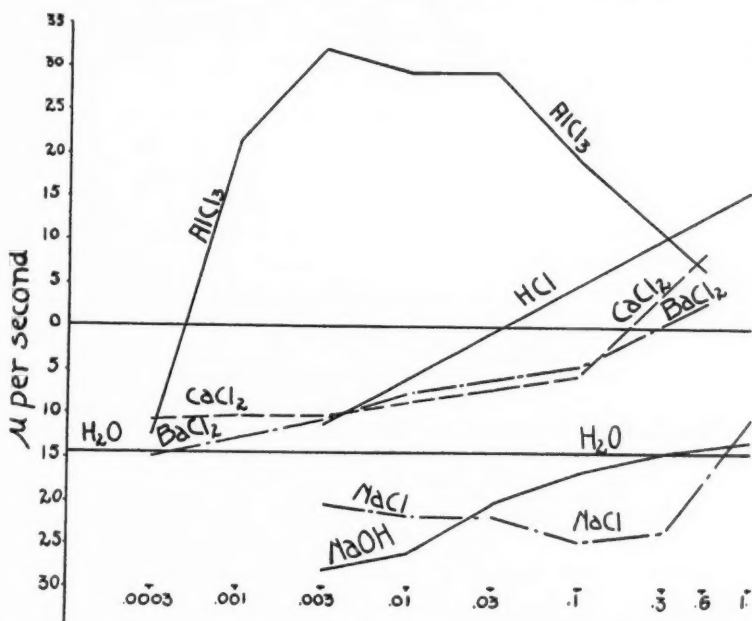


FIG. 4. RATE OF MIGRATION OF KAOLIN PARTICLES IN $\pm \mu$ PER SECOND WHEN EFFECTED BY MOLAR CONCENTRATIONS OF ELECTROLYTES

of the physical nature of the electrolyte in retarding the particles. The true speed of the particles is believed to be somewhat decreased. Then, too, the size of the particles varies in different solutions and the mass of the particles introduces an error. It was only with the greatest difficulty that any figures at all could be obtained for HCl. This acid appears to neutralize the charge of the particles very completely, causing no motion whatever in most cases, although the particles remain suspended. It was clearly seen that in the same solutions at any given level, particles migrated to both the anode and cathode. Indeed the same particle could change the sign of its charge several times before passing from the field of the microscope.

As before mentioned, it is impracticable to calculate the intensity of the charge because the particles have no definite size or shape and they may form aggregates of varying complexity. The intensity of the charge is here measured by the speed of migration of only those particles which move. This introduces still another error in observations made on slow moving particles. Results are comparative and are presented only as such.

Figure 4 illustrates the effects of the various ions on the charge of the particles. It is evident that NaOH increases the charge to the greatest extent in the negative direction and that NaCl does not have quite so pronounced an effect. Ba, Ca and HCl decrease the charge and in dilute solutions, as does Al. But Al rapidly neutralizes the charge and even in dilute solutions reverses it to a marked extent. Only the most concentrated solutions of Ca and Ba reverse the charge of the particles, and HCl is more efficient in this regard than Ca or Ba. Increasing the concentrations of NaOH and NaCl decreases the charge of the particles. But this effect, as before pointed out, may be due to the internal friction of the solutions. When the concentration of Al is increased beyond 0.003 *M*, the charge is also decreased.

It was thought that some correlation between the intensity of the charge on the particles and the final volume of the sediment could be obtained from these experiments. That the degree of flocculation is independent of the sign or intensity of the charge is apparent from a comparison of the curves of figures 1 and 4. On the contrary, with Al, it seems that as the charge increases, the final volume of the sediment increases, but this statement does not hold for the other electrolytes. This condition is at variance with suspensions of the metals where the intensity of the charge determines the amount and speed of precipitation. There does seem to be some correlation between the intensity of the charge in either direction and the turbidity of the solution. Table 1 shows this quite clearly. It appears that flocculation with kaolin depends on the quantity and quality of the supernatant liquid. Calcium acts as a deflocculating agent on "chemically pure" kaolin as compared with the final volume of the kaolin in distilled water, although it decreases the charge on the particles. This statement is quite at variance with the generally accepted view.

DISCUSSION

Calcium is generally regarded as a flocculating agent in soils. The data presented indicate that it is a deflocculating agent on kaolin. There is no discrepancy in the two statements when it is considered that this paper deals with high resistance kaolin. Mattson (16) in discussing this question is of the opinion that calcium acts as a binder, or bridge between two particles of clay, holding them together. The number thus held increases with the pH, in this way hastening flocculation of the soil in question. It is believed that any effect that Ca may have as a flocculating agent is due only to the reduction in the effect produced by some electrolyte already present which has

deflocculated the soil to a greater extent than calcium is capable of doing. There is also the possibility of the precipitation of the hydrates of aluminum and iron, in this way binding together many clay and sand particles. Then too the flocculating effect of calcium on soils probably is not due directly to the effect on the soil particles but indirectly by the precipitation of silicates and humates.

The cataphoretic measurements reported by Dayhuff and Hoagland (5) in working with clay suspensions show the same general tendency as those given here. They say, in part,

within the range of reaction found in the soil solutions, the clay colloid . . . showed no change in the sign of its electric charge, and the nature and concentration of the cations present in the solution had a predominant influence on the stability of the colloidal suspension.

The observations of Dayhuff and Hoagland are in harmony with the present findings, with the single exception that 0.8 milliequivalents of aluminum as the chloride show a pronounced positive charge with kaolin. This is believed due to the greater purity of the kaolin used over the clay suspension of Dayhuff and Hoagland.

As before pointed out, HCl is adsorbed at all concentrations used and the nature of the curve indicates that HCl would be adsorbed even at infinite dilution. No other electrolyte used was adsorbed at dilute concentrations, but were "negatively adsorbed." The data presented indicate the "negative adsorption" sequence: NaCl, NaOH > Ba > Ca > Al.

The pH of the AlCl_3 solutions is very low. The hydrolysis of this salt would result in the liberation of a strong acid and a very weak base. It is then possible that it is the HCl which is adsorbed and not the molecule of the salt. The pH of the chlorides of calcium and barium is much higher, and adsorption does not begin until the solutions are comparatively concentrated. The hydrolysis of NaCl would result in the liberation of an equally strong base and acid, and as demonstrated by the curves, NaCl is least adsorbed by kaolin. It is unfortunate that pH determinations were not sufficiently accurate to indicate consistently the adsorption of the acid. Interpreted in this way, however, adsorption results are in accord with the work of Miller (19). In working with sugar charcoal, he comes to the conclusion that strong inorganic bases are "negatively adsorbed" and that adsorption from solutions of some salts is exclusively hydrolytic in nature, whereas from others, it is partially hydrolytic and partially molecular. Such conclusions are in accord with the theorem of Gibbs, that substances lowering the surface tension of a liquid are positively adsorbed at an interface, whereas those raising the surface tension tend to keep from the surface. This "negative adsorption" effect does not increase with the concentration. HCl decreases the surface tension of water whereas the other electrolytes used increase it. The work of Miller seems sufficient to explain the curves of figures 2 and 3.

In this regard, it is suggested that the theories of Harkins (7) together with the fixation effects of Langmuir's (11, 12, 13) secondary or residual valencies furnish some explanation of the phenomena of adsorption by kaolin. However, the data here presented are not sufficient to test their applicability.

From the above discussion, it would seem that adsorption is a function of pH and, as Loeb (14) has pointed out in his work on gelatine, when the pH is kept constant, there is no Hofmeister series. That his observations do not apply in the case of kaolin is apparent from figures 1 and 4. There can be no correlation between pH and flocculation when the curve for HCl is compared with any of the others, the flocculating tendency is the same, but the degree is vastly different. In the migration of the particles, neither the degrees nor the tendencies are similar.

There can be little question that each ion has its own specific effect on the particles with regard to degree of flocculation or deflocculation. That this affect is produced in the most dilute solution used is demonstrated by the curves of figure 1, despite the fact that the electrolytes used (HCl excepted) are "negatively adsorbed" at those concentrations.

The writer knows of no explanation that can adequately account for the phenomena described and only ventures the suggestion that Gibbs' Theorem is operative as described by Harkins and Miller, and that the effects of specific ions are due to their fixation to a greater or less extent at the surface because of the secondary of residual valencies described by Langmuir.

Figures 2 and 3 show conclusively that in the salt concentrations found in the soil, that is, concentrations of less than 0.003 *M*, the essential ions are not adsorbed by the particles of kaolin. At least, if any adsorption occurs at these concentrations, it is a negligible quantity. As Bouyoucos (2) has pointed out, this fact is opposed to the prevalent notion. He states in part,

experimental evidence . . . proved the opposite view, namely, the solution around the soil particles and in the very fine capillary spaces is less concentrated than the mass of the solution. All experimental evidence obtained is overwhelmingly in favor of this view.

SOLUBLE AND AVAILABLE ALUMINUM IN THE SOIL

From the data presented, it is clear that particles of clay are in a partially deflocculated condition at neutral pH and are progressively deflocculated as the pH increases. This statement is believed to apply only to soils with a high clay content. This is the only conclusion tenable in view of the successive solubilities of the mono-, di-, and tri-valent bases with decreasing pH. Another way of stating the condition, is that the soil is progressively flocked with increase in acidity. This flocculation, as before pointed out, is not due to the H-ion but rather to the ions brought into the soil solution as a result of the increasing acidity. It follows then that aluminum and iron are present in the soil solution in an easily soluble form in significant quantities at pH below 5.00.

In an effort to demonstrate that aluminum was present in significant quantities in solution at pH of from 4 to 5, the following experiment was performed.

Stock solutions were prepared and determined and the following nutrient solutions were made by dilution:

Ca (NO ₃) ₂	0.016 and 0.008 <i>M</i>
MgSO ₄	0.008 and 0.004 <i>M</i>
H ₃ PO ₄	0.02 and 0.01 <i>M</i>
Al ₂ (SO ₄) ₃	0.002 and 0.001 <i>M</i>

To change the pH, a liter of the above nutrient was titrated with standard KOH. The curves are of exactly the same type as Clark (4) found in the titration of H₃PO₄ with normal KOH. The greatest value of the tangent is reached between pH 3.8 and 5.2. The exact amount of Al added per liter being known, analyses were made to determine the amount precipitated at various acidities. Insofar as no Fe was added, Al determinations could be made directly after separating off the Mg and Ca. To lose as little Al as

TABLE 2
Effect of dilution on Al solubility

pH OF NUTRIENT	Al IN SOLUTION	
	2 X concentration	X concentration
	<i>p. p. m.</i>	<i>p. p. m.</i>
4.35	6.0	6.5
4.53	3.7	4.0
4.70	2.3	2.1
4.85	0.9	...
5.42	1.1	...

possible, the volumes were kept down to less than 75 cc. and precipitates were washed with as little water as possible, tests being made for Ca and Mg constantly. The pH of the precipitating reactions were kept below 7.0.

Analyses of the precipitate formed showed in both series practically the same amount of Al in solution. From table 2 it may be seen that dilution has no apparent affect on Al solubility.

The Al in solution could not possibly have any effect on the soil or kaolin particles with regard to their flocculation. Even if the method of analysis employed is assumed to give 100 per cent error, the quantities of Al in solution could cause no flocculation of the kaolin.

A search for the reason brought to light several articles that had been overlooked. A comparison of the determinations made by Magisted (15) for Al present in solution indicates that the quantity of soluble Al in solution is a function not only of pH but of PO₄ as well. Crone's nutrient, high in phosphoric acid, renders Al more insoluble, whereas the nutrient of Hartwell and Pember with only a small molar concentration of phosphoric acid equiva-

lent, increases the solubility of Al over that found in the nutrient reported in this paper.

Whether this view is the correct one can only be determined by further work. However, the experiments of Mirasol (20) indicate that this opinion is true. He found that the addition of acid phosphate reduced the toxicity of Al to plants and that the decrease in toxicity depended on the rate of acid phosphate application. Hartwell and Pember (8) observed that the amount of active Al is decreased by the increase of acid phosphate application despite the increase in the acidity of the soil so treated. From the determinations of Burgess (3) and Mirasol it seems that aluminum is present in the soil at low pH, not as the phosphate (unless phosphate was added) but as the nitrate, sulfate, or chloride. From their data it also seems that the quantities present depend on the nature and antecedents of the soil.

In order to obtain some estimation of the quantity of aluminum and iron present in the solution of the soil before reported upon (22) in connection with the formation of hardpan, the method employed by Blair and Prince (1)

TABLE 3
Analysis of 1 liter water extract from four soil samples

SOIL SAMPLE	pH	COMBINED ALUMINUM AND IRON
		<i>p.p.m.</i>
1	4.5	52
2	4.75	45
3	5.0	5
4	5.2	12

was used. Table 3 shows the results obtained by the analysis of 1 liter of the water extract obtained from 5 kgm. of four soil samples.

Two samples were taken from the southern part of the area in which hardpan was found, the pH being 4.5 and 4.75; and two samples were taken from the part of the area where hardpan was not found, the acidities being 5.0 pH and 5.2 pH.

The southern part of this area is greatly affected by quantities of smoke from neighboring factories and railroads.

This is believed to be the proof needed to support the theory of hardpan formation to be advanced. A comparison with the results of Blair and Prince show these values to be considerably higher than they obtained. Furthermore, soils 3 and 4 do not fall on a theoretical curve that can easily be imagined. It is probable that this is because of different quantities of phosphate present in those soils.

A THEORY FOR THE FORMATION OF HARDPAN IN ACID CLAY SOILS

The theories advanced relative to the formation of such hardpans have been based almost entirely upon the mechanical behavior of the soil parti-

cles—surface drying, precipitation of various cations because of supersaturation, the carrying down of small particles, and so on. These factors undoubtedly play a part, but in themselves are not sufficiently in accord with the facts observed in the case. Some years ago Warington (26) observed:

Hydrated ferric oxide is another colloid substance which in sandy soils undoubtedly plays the part of a cementing agent. In rocks and soils of the Red Sandstone formations, its influence is plainly marked. Perhaps, however, the most obvious example of the cementing action of ferric oxide is afforded by the formation of iron-pan in Moor soils. . . . The iron has been dissolved out of the surface soil by the action of humic acids . . . passes in solution into the subsoil where it is precipitated, with the result that the sand at a certain depth is cemented together and an iron-stone produced.

Warington had little evidence in support of this view other than observation and did not mention that the same phenomena could obtain in clays as well. The evidence presented here supports his view and attempts to explain just how that layer comes into being.

It has been shown in the weak concentrations found in the soil solution that the essential salts necessary for plant growth are kept away from the surface of the clay fraction. This is in accord with the Second Law of Thermodynamics and the Theorem of Willard Gibbs. That the effects of the various cations in these concentrations, despite apparent non-adsorption, is evident has also been shown. The explanation suggested is that the residual valencies induce a weak chemical attraction such as Langmuir pointed out. HCl is greatly adsorbed by kaolin and according to Miller, this applies to other acids in the case of sugar charcoal. As shown in final volume of sediment curves, both HCl and Na_2SO_4 greatly deflocculate kaolin as compared to water. The tri-valent citrate ion is still more efficient in this regard. That mineral acids are present in the soil has been demonstrated by many workers.

Na and K are soluble at the lower acidities. As the pH decreases, calcium and magnesium are leached from the soil solution. This loss results in a further decrease in the pH which brings into the soil solution iron and aluminum. From the data presented, it is evident that at the lower pH, iron and aluminum do not generally exist as the phosphates in which condition they are insoluble. Rather they are present as chlorides, nitrates, or sulfates.

The hardpan observed and previously reported upon indicated that the first cause in its formation was the deposition of SO_2 blown by the prevailing winds across the area from factories and railroads. The closer to the railroads and factories, the more prevalent and well defined was the hardpan. It is reasonable to suppose that the decreased pH was due to the formation of sulfuric acid.

With regard to the clay fraction, deflocculation prevails at the higher pH because of the high molarity of the soil solution in salts that can dissociate clay aggregates. Undissociated particles are constantly being washed down by gravitational water and are deposited at various depths, depending on the mechanical condition of the soil. Attending this phenomena is the fall in

pH, and the pH increases with the depth of the soil. Kelly (10) has shown that the lowest pH is generally at a depth of five or six inches from the surface. Thus the surface soil will lose sodium and potassium, and latterly, magnesium and calcium to the soil at greater depths. The result is that the clay particles are carried farther and farther down because of deflocculation.

When the acidity at the surface is sufficient to bring into the soil solution aluminum and iron, the formation of a hardpan layer begins. This pH is something less than 5.0, but may be slightly higher depending possibly on the phosphates present.

The iron and aluminum in dilute solutions are not adsorbed by the clay and so in the soil solution are carried down and with the decrease in acidity are deposited farther from the surface. The progressively decreasing pH results in more and more iron and aluminum being brought into the solution until sufficient quantities are present to cause the flocculation of the collected dispersed clay particles at some depth, depending on the pH.

The aggregated clay particles cause the formation of a tight layer very slowly permeable to water. When this layer has dried out, aluminum and iron are deposited around the aggregates as the oxides, mechanically binding the entire mass together and effectively preventing the passage of water.

The analyses of the soil, where the hardpan was found, for combined aluminum and iron show that there is the equivalent of approximately .0015 M $AlCl_3$ present. Figure 1 shows that considerably less than this concentration brings about the maximum flocculation of kaolin and also that at about this concentration aluminum is adsorbed. At the part of the same area of ground where no hardpan was found, the equivalent of less than 0.00004 M $AlCl_3$ was analyzed.

These figures may also be interpreted as indicating the toxic properties of soluble aluminum.

SUMMARY

Kaolin being used as criteria for all clays, determinations have been made on the degree of turbidity of a supernatant solution, on the final volume of the sedimented kaolin when treated with various solutions, on the conductivity of solutions for adsorption data, and on the sign and intensity of the charge on the particles. These experiments are preliminary and the data are only presented for their comparative value.

Several concentrations of HCl , $NaOH$, $NaCl$, Na_2SO_4 , $C_2H_5(COONa)_3$, $BaCl_2$, $CaCl_2$, $AlCl_3$, sucrose, and urea were used.

Different concentrations of the same electrolyte affect turbidities to a marked extent. Al clears the supernatant liquid in dilute solutions immediately after shaking, whereas the citrate and sulfate ions stabilize the suspension.

There is some correlation between turbidities and the final volumes of sediment. The most turbid solutions generally decrease the final volumes of

the kaolin to a marked extent, whereas nearly all the solutions of Al greatly increase the final volume.

Sucrose and urea have no effect on the kaolin whatever.

Of the ions used, Al and Na alone cause flocculation.

HCl is adsorbed at all dilutions to a great extent.

No other electrolyte used was adsorbed by the kaolin in the more dilute solutions.

A "negative adsorption" sequence is obtained: NaCl , NaOH > BaCl_2 > CaCl_2 > AlCl_3 .

In concentrated solutions Al, HCl, and Ca and Ba reverse the sign of the charge on the particles most efficiently in the order given.

The degree of flocculation is apparently independent of the intensity of the charge on the particles.

Evidence is presented in support of the view that adsorption is not a function of pH in clays.

From the findings it seems that the amount of Al in a soluble form in the soil moisture depends on the amount of phosphate present in that soil as well as on the pH. That is, a great decrease in either may result only in a slight increase in the amount of Al present; a slight decrease in both will cause a great increase in the amount of Al and Fe in solution.

A theory is advanced to account for the formation of hardpan in acid clay soils.

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DIFFERENCES IN THE HEAT OF REACTION BETWEEN ARTIFICIAL AND SOIL GELS OF SILICA, ALUMINA, AND IRON, WITH HYDROXIDES

GEORGE JOHN BOUYOUCOS

Michigan Agricultural Experiment Station

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While various studies on the heat of wetting of soils with water (1), were being conducted, the idea was suggested of investigating also the heat of reaction between soils and various chemical compounds. Accordingly, a series of studies was undertaken to ascertain whether there was any heat of reaction between various soils and different chemical compounds, and if so, measure the magnitude of this heat of reaction. Salts and hydroxides were employed. It was found that there was no measurable heat of reaction between the soils and salts, but that there was with the hydroxides, especially KOH and NaOH. A rather extensive study was then made of the heat of reaction of various soils with these hydroxides. In addition to the soils, soil colloids and artificial gels of silica, alumina, and iron were also used for purposes of comparison. The results obtained showed that whereas all the soils and soil colloids gave a considerable heat of reaction with the hydroxides, some of the artificial gels, especially silica, gave, in comparison, an enormous heat of reaction with the same hydroxides. For instance, the heat of reaction between silica gel and 3 N KOH was 146.7 calories per gram of material, whereas the highest value obtained in soils or colloids, excepting organic matter, was only 6.5 calories per gram. This is certainly an enormous difference, and raises many questions as to the similarity or dissimilarity in the physical and chemical characteristics of the gels of silica, alumina, and iron as they exist in the soil colloids and in the artificial state. It is the object of this paper, therefore, to present the data which show in detail the differences in the heat of reaction between soils, soil colloids, and artificial gels, with hydroxides.

PROCEDURE

The procedure followed in measuring the heat of reaction of materials in hydroxides, was essentially the same as that employed in determining the heat of wetting of soils with water, described in previous communications (1).

The total heat generated by the materials in the hydroxides included both the phenomenon of heat of wetting, and the heat of reaction. To obtain the latter, therefore, the heat of wetting with water was also determined and subtracted from the total for each respective material.

Four different hydroxides with various concentrations were tried, but the results of 3 *N* KOH and 3 *N* NaOH only will be given here.

EXPERIMENTAL DATA

In table 1 are presented the data on the heat of reaction of various types of soil, different soil colloids and artificial silica gel, alumina gel, and iron hydroxide.¹ For purposes of comparison, the heat of wetting of each material is also shown.

TABLE 1
Heat of wetting with water and heat of reaction with KOH and NaOH of soils and artificial gels

MATERIALS	HEAT OF WETTING WITH WATER	HEAT OF REACTION WITH KOH	HEAT OF REACTION WITH NaOH
	calories per gram	calories per gram	calories per gram
Freno fine sandy loam.....	1.12	0.17	
Amarillo fine sandy loam.....	4.97	0.43	
Rhode Island sandy loam.....	2.62	5.29	4.21
Ohio silt loam.....	2.109	1.15	1.12
Tennessee silt loam.....	2.45	2.48	1.62
Pennsylvania silt loam.....	2.81	1.58	1.48
Michigan silt loam.....	3.00	3.29	2.45
Michigan silt loam.....	1.55	1.91	1.81
Chester loam.....	2.39	1.11	0.95
Michigan Clay loam.....	4.98	3.72	2.52
Illinois Urbana Clay loam.....	4.00	3.92	2.18
California Yolo clay.....	6.52	3.52	1.94
Red clay—calcareous.....	2.81	2.01	1.12
Clay—calcareous.....	4.00	1.65	1.01
Ontonagon silt loam A ₁	3.94	5.09	3.76
Ontonagon silt loam A ₂	4.23	5.74	4.23
Ontonagon clay B ₁	6.50	4.26	2.28
Colloids from Ontonagon silt loam A ₂	7.51	5.89	
Colloids from Ontonagon Clay B ₁	9.12	4.62	
Colloids from Illinois Urbana clay loam.....	8.48	4.21	
Colloids from California Yolo clay.....	11.02	4.02	
Muck.....	29.50	25.82	20.14
Ferric hydroxide gel.....	9.390	13.65	
Alumina gel.....	21.95	61.23	
Silica gel.....	24.50	146.70	

The data in table 1 reveal many significant and interesting things. In the first place it is readily seen that all the materials employed gave a heat of reaction both with KOH and NaOH and that the magnitude of this heat of reaction varies tremendously with the different materials, especially between the soils and soil colloids, and the artificial gels. The magnitude of the heat of

¹ These three gels were kindly furnished by the Chemical Warfare Service.

reaction with KOH—in which the data are more complete—varies in the case of soils, from 0.17 calories in Fresno fine sandy loam, to 5.74 in Ontonagon silt loam A₂ horizon, to 28.50 in muck. In the case of soil colloids, it ranges from 4.02 calories in California Yolo clay to 5.89 in Ontonagon silt loam A₂ horizon. In the case of the artificial gels, it is 13.65 calories for ferric hydroxide gel, 61.23 for alumina gel, and 146.70 for silica gel. The differences between the figures for artificial gels and soils and even for the colloids, are certainly very great. The rather surprising thing is that the soil colloids gave no greater heat of reaction than the soils from which they were extracted. As will be seen the amounts are about the same in both cases.

The heat of reaction with both the KOH and NaOH does not vary in any constant manner in the different soils. Since muck gave a very great heat of reaction, it would logically seem that soils containing a high content of organic matter would give a correspondingly high value of heat of reaction. Such would seem to be the case, as in Rhode Island sandy loam and Urbana clay loam, but there are some cases in which the heat of reaction is comparatively high, but which contain hardly any organic matter. For instance, Ontonagon B₁ horizon contains practically no organic matter and yet it gives a greater heat of reaction than the majority of the soils investigated. The possible reason for these differences will be discussed.

NaOH gave a lesser heat of reaction than KOH with every material employed. The values are also irregular in the different soils.

A comparison next, of the heat of wetting with water with the heat of reaction with the hydroxides in the respective materials, shows that, with the exception of one case in the soils and one case in the soil colloids, the heat of wetting is greater than the heat of reaction with either KOH or NaOH, and that in many cases the differences in favor of the heat of wetting, are appreciable. For instance, the heat of wetting of Amarillo fine sandy loam is 4.97 calories, whereas its heat of reaction with KOH is only 0.43 calories. In Yolo clay, the heat of wetting is 6.52 calories, whereas its heat of reaction with KOH is 3.52 calories. In muck the heat of wetting is about the same as the heat of reaction with KOH, but much higher than that with NaOH. In the case of the artificial gels, however, the heat of reaction with KOH is far greater than the heat of wetting, especially in the case of the alumina and silica gels.

Again, a comparison of the heat of reaction between the soil colloids and the artificial gels, raise the question: Why should the heat of reaction in the soil colloids not be as great as that in the artificial gels, since, the chief constituents of the soil colloids consist of iron, alumina, and silica? The recent work of Robinson and Holmes (2), which contains the chemical analysis of a large number of colloids representing diverse types of soils throughout the United States, shows that the soil colloids are composed mainly of silica, alumina, and iron oxide, and that the silica may vary from 31.84 to 55.44 per cent, the alumina from 16.42 to 38.28 per cent, and the iron oxide from 4.66 to 16.67 per cent. If the silica, alumina and iron in the soil colloids were

in the same chemical and physical constitution, it would logically seem that they would react the same as in the artificial state. The fact that they do not react the same with the hydroxides, indicates that they are probably not of the same constitution. This heat of reaction could be caused by any one or by all of the following factors: (a) solution, (b) neutralization, (c) adsorption. The second and third factors could be of predominant importance, but in the present instance, they are negligible. It is the first factor that seems to be the main, if not the sole, cause of the heat of reaction manifested in the different materials with hydroxides. For instance, in the case of the artificial silica gel and the muck, which give the greatest amount of heat of reaction, it is actually seen that the materials have been dissolved and are in solution. This is especially true in the case of silica gel. It would seem, therefore, that the larger the amount of material dissolved, the greater will be the heat of reaction. The silica, alumina, and iron are apparently not of the same constitution in the soil colloids as in the artificial state, and cannot be dissolved as readily, and consequently their heat of reaction is less. Hence, this seems to be another evidence that the constitution, at least the physical constitution, of the soil colloids, is not the same as that of similar materials in the artificial state.

The differences in the heat of reaction obtained in the various soils could be explained, therefore, on the basis that different amounts of silica, alumina, iron, and organic matter are dissolved in the various soils.

It is of interest to note here that the heat of wetting gives values which are quite close to those of the artificial gels. For instance, in a former communication (1), it was shown that many soil colloids gave a heat of wetting as high as 16.192 calories (California adobe clay) as compared with 24.5 calories in silica gel. From the results with heat of wetting, it would seem that the silica, alumina, and iron gels in the soil colloids were very similar, but the results with the heat of reaction makes them appear radically different.

SUMMARY

When soils, soil colloids, and artificial gels of silica, alumina, and iron are treated with KOH and NaOH, heat is generated. This is the heat of reaction, which is in addition to that of heat of wetting.

The amount of heat of reaction in soils and soil colloids is rather small, whereas that in the artificial gels is comparatively tremendously high. In the mineral soils and soil colloids, it varies with KOH from 0.17 to 5.89 calories per gram of material; whereas in muck, it is 29.50 calories; in ferric hydroxide gel, 13.65; in alumina gel, 61.23; and in silica gel, 146.70. Apparently the difference in the heat of reaction between the artificial gels and the soil colloids is very great.

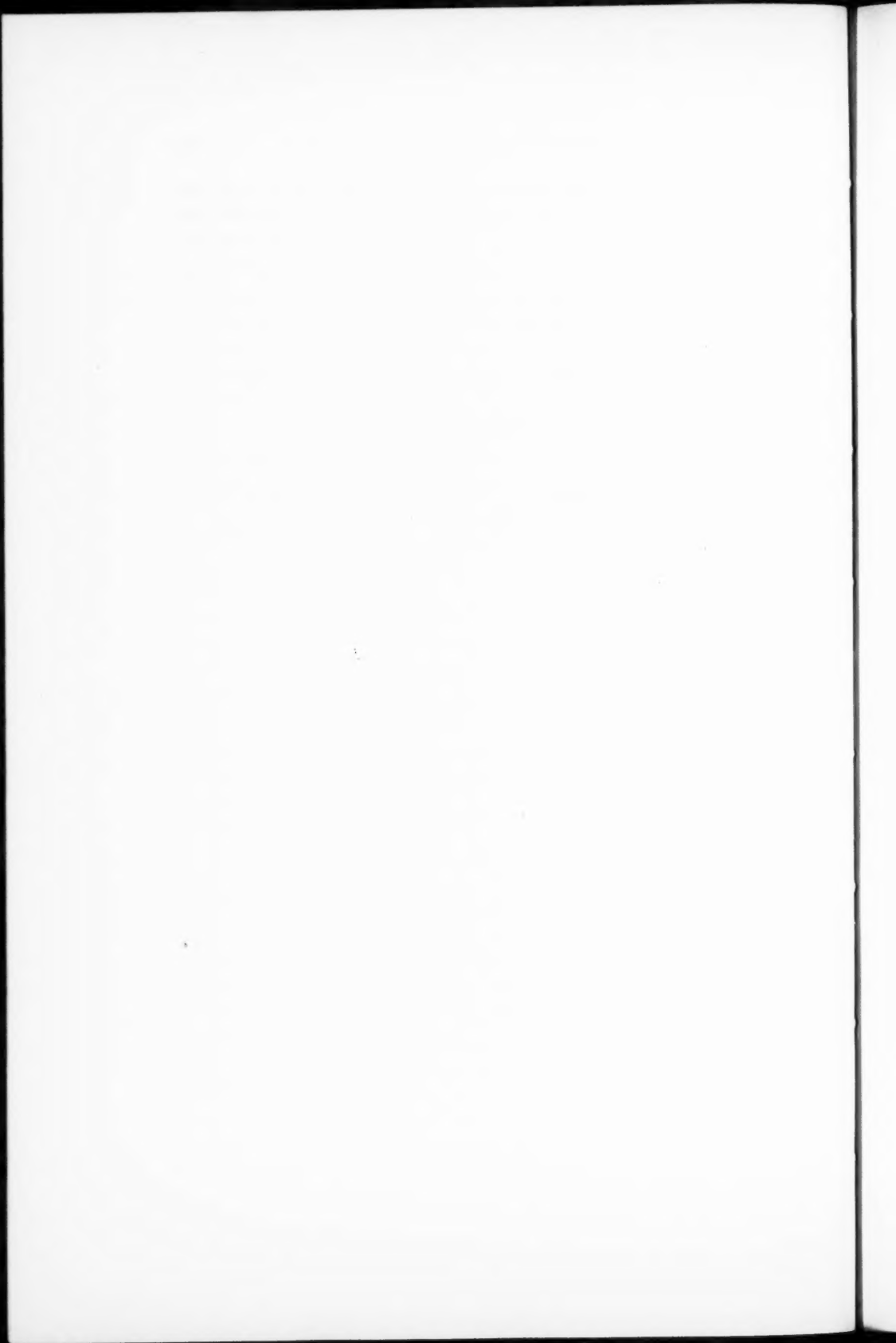
This heat of reaction seems to be due mainly to the dissolving effect of the hydroxides upon the materials. It is actually seen that all the artificial silica gel goes into solution.

Considering that the soil colloids are composed chiefly of the same gel constituents employed in this investigation; namely, silica, alumina, and iron, and yet they gave a very small amount of heat of reaction as compared with that of the artificial gels, it becomes evident that the silica, alumina, and iron in the soil colloids probably do not have the same constituents as in the artificial state. These results may be considered as additional evidence that the gels in the soil colloids are not be in the same condition as in the artificial state.

On the other hand, the heat of wetting values, as shown in previous works, does not show the soil colloids and artificial gels to be radically different.

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BOOK REVIEW¹

Plant Nutrition and Crop Production. By E. J. RUSSELL, University of California Press, Berkeley, 1926. ix + 115 pp., 37 fig., 21 pl.

This little volume consists of a series of lectures delivered in 1924 under the auspices of the Hitchcock foundation at the University of California, by the eminent scholar Sir John Russell, Director of the Rothamsted Experiment Station at Harpenden, England.

These lectures are a valuable addition to the efforts of the workers in scientific agriculture to elucidate the complex problems of plant environmental relationships in the light of our modern knowledge of chemistry and physiology. The title of the volume, "Plant Nutrition and Crop Production," may well be amplified by "a scientific inventory of the complex plant-soil system," for indeed it is a successful attempt to bring together the achievements of the scientific workers in the realm of agricultural sciences in establishing the fundamental relationships between plants and their environment.

A superficial examination of these lectures may mislead one into considering them a digest of the author's monograph, "Soil Conditions and Plant Growth." Although there is of necessity some repetitions, the subject under consideration is amplified with the most recent contributions of the rapidly growing knowledge of the physico-chemical and biological laws governing plant-soil reactions and behavior.

The first chapter—"The Study of Plant Nutrients"—deals primarily with the historical development of our knowledge of the "sources from which plants derive their substances." A skilful, short review of the earliest ideas on the subject ushers us in into the nineteenth century with an analysis of the contributions of de Saussure and Boussingault; these are followed by a critical review of the "turning point in the history of agricultural science," the researches of Liebig. Next come the classical experiments of the Rothamsted workers, the dawn of the fertilizer industry and practice and the principle involved. This leads the author to review briefly the fertilizer industry and the important fertilizer investigations in Europe and in the United States.

In the second chapter—"Positive Science and Exact Demonstration"—the author discusses the Mitscherlich logarithmic curve, which expresses the basic assumption that "the increased yield produced by increments of a nutrient is proportional to the decrement below the maximum producible if the nutrients were present in excess." He also presents some of the statistical data of Fisher from the Rothamsted Station "in an attempt to give quantitative

¹ This review was prepared by J. S. Joffe, of the New Jersey Agricultural Experiment Station.

expression to the facts of plant nutrition and growth." The timely subject, the rôle of farmyard manure in agriculture, is also interestingly discussed in the second chapter. The author seems to lean toward the view that organic matter cannot be replaced entirely by artificial manures. He is inclined to believe that the organics have a specific function outside of their value as improvers of tilth and moisture-holding capacity. This theory, which finds support in the experiments of Bottomley, is that organics possess a certain positive effect on plant growth which cannot be produced by artificial nutrients.

The third chapter—"Decay and the Living Plant"—is a discussion of the transformation of organic matter and of the nitrogen cycle. It takes up the rôle of specialized groups of microorganisms in the decomposition process of organic matter, the energy relationships and the carbon nitrogen ratio. The author attributes the direct microscopic method to Winogradsky, omitting the earlier work of Conn from the Geneva Station, United States, to whom Winogradsky gives due credit.

The last part of this chapter is a preamble to the fourth chapter—"The Soil Microorganisms; Can They be Controlled and Utilized?" This is a discussion of the methods used in controlling the various functions of the soil flora. The subject of soil inoculation, of course, is dealt with. A good share of this chapter is devoted to a discussion of the process, developed at the Rothamsted Station, of making manure from straw and other organic waste products by the addition of proper nutrients and by maintaining favorable conditions for the activities of microorganisms. The author did not discuss fully the subject of the soil population, but such omissions, as for instance autotrophy in soils, are probably a result of time limitations.

In the concluding chapter—"The Soil and the Living Plant"—Russell skims over the process of soil formation. He recognizes three divisions: first, the lateritic and silicate soils; second, the one that is determined by the presence or absence of calcium; third, that depending on the fate of the organic matter. A considerable discussion of soil colloids and base exchange is given.

The study of the soil complexes is one of the most fascinating problems for the future. The present investigations on basic exchange may reveal a good deal, but there are even greater hopes from the application of physical methods. It is possible that the use of X-rays might teach us as much about the structure of soils as in the hands of Sir William Bragg and his son they have taught about the structure of crystals.

There is also a brief discussion of soil moisture and gases in relation to plant growth.

A series of graphs, charts, and plates illustrate the points brought out in the subject matter.

A RESEARCH PROFESSORSHIP IN FOREST SOILS AT CORNELL UNIVERSITY

A gift of \$130,000 for the endowment of a research professorship in forest soils in Cornell University has been announced by President Livingston Farrand, who said that the Charles Lathrop Pack Forestry Trust, founded by Mr. Charles Lathrop Pack, President of the American Tree Association, in addition to endowing the chair, had made a further generous provision of funds for the operating expenses of the advanced line of investigation to be undertaken.

The work will be done in the New York State College of Agriculture, and the appointment of the professor will be announced shortly, President Farrand said. The chair will be named for Mr. Pack.

"In the northeastern hardwood area, extending over the Middle Atlantic States and as far west as Indiana and Illinois, the question of proper forest care and operation depends very largely upon a study of soil conditions, and practically no data on forest soils are at present available," President Farrand said. "The proposed line of investigation is a new development in forest research in this country. It will undertake to coördinate studies in several fields of science and apply what is learned to the special soil problems involved in the business of growing healthy forests.

"This research will necessarily deal with the chemistry and biology of soils. It will naturally have intimate relation with the field of heredity in tree growth, particularly as it should help to solve problems of adapting certain varieties of trees to given soils. And it will similarly have a bearing on the field of plant pathology, because of the relation that soil conditions bear to diseases of trees.

"Many of the timber grower's problems are complex. Their solution must be looked for in several fields, including these interrelated fields of soils, genetics, and forest pathology.

"This is the first time that such a comprehensive research on forest soils has been systematically undertaken in this country. The comprehensive study of forest soils is a new line of research everywhere, and the only specialized workers in it are a few scientists in Sweden, Russia, Finland, and Germany. Although the work to be done under Mr. Pack's endowment will deal directly with American forest problems, its results will have international interest and general scientific value."